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Modular Synthesis of Highly Substituted 3-Azapyrroles by Rh(II)-Catalyzed N−H Bond Insertion and Cyclodehydration

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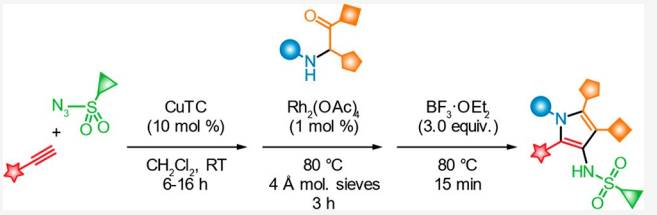
ABSTRACT: A modular synthesis of highly substituted 3-azapyrroles has been developed using a three-step sequence comprising copper-catalyzed alkyne−azide cycloaddition (CuAAC), N−H bond insertion, and cyclodehydration. 1-Sulfonyl-1,2,3-triazoles (1-STs) can be accessed from common alkyne and sulfonyl azide building blocks by CuAAC using CuTC. Rhodium(II)-acetate-promoted 1-ST denitrogenation results in highly electrophilic rhodium azavinyl carbenes that, here, underwent insertion into the N−H bond of secondary α-aminoketones to form 1,2-aminoalkenes. These products were cyclized and dehydrated using $BF_3{\cdot}OEt_2$ into highly substituted 3-azapyrroles. The three steps (CuAAC, N−H bond insertion, and cyclodehydration) could be telescoped into a one-pot process. The method proved to be highly efficient and tolerated a wide range of substituents.



INTRODUCTION

Pyrroles are ubiquitous five-membered nitrogen-containing heteroaromatic compounds that display valuable properties, making them key fragments in a wide variety of natural products,[1] pharmaceuticals,[2] and functional materials.[3] Several valuable pyrroles have 3-aza substitution, including the DNA minor groove binders netropsin[4] **1** and distamycin A[5] **2** as well as other natural products such as geranylpyrrol **3** (Figure 1).[6]

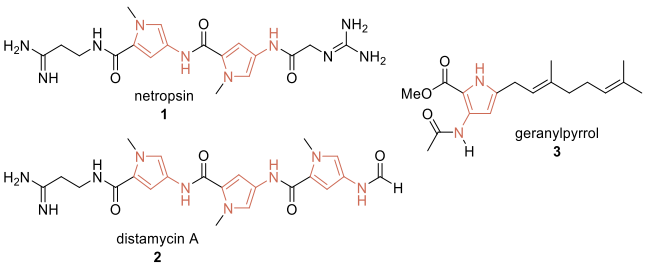


Figure 1. Selected biologically active 3-azapyrroles.

The value of pyrroles has inspired many synthetic approaches spanning the whole history of organic chemistry.[7] However, these established methods are not always easily adapted to the synthesis of 3-azapyrroles.[8] Therefore, development of novel synthetic strategies toward this privileged heterocycle is necessary. Ideally, newly developed methods should begin from cheap and readily available starting materials and be straightforward to carry out practically, highly atom efficient, modular, and tolerant of a wide range of functional groups.

The reactivity of 1-sulfonyl-1,2,3-triazoles **4** (1-STs) has been developed such that they can be considered readily accessed building blocks[9] for the facile synthesis of a wide range of value-added products.[10] The sulfonyl group provides an ideal balance to the triazole heterocycle, bringing stability but also allowing on demand reactivity when an appropriate catalyst system is deployed. The majority of examples of this strategy involve triazoles and rhodium(II) carboxylate catalysts, although, recently, palladium(0) catalysts have shown analogous reactivity with 1-trifluoromethanesulfonylbenzotriazoles **5**.[11]

The key reactivity of 1-STs arises from the catalyst promoting Dimroth equilibration and denitrogenation of the nitrogen-rich heterocycle to give a highly reactive organometallic intermediate **6** (Scheme 1). In terms of reactivity, the organometallic species **6** can be considered as a three-atom ylidic synthon **7** with its positive component on the carbon and negative component on the nitrogen atom. Therefore, reaction with a suitable two-carbon π component results in the formation of a new five-membered nitrogen heterocycle **8**, i.e., a pyrrole, indole, or reduced version thereof. This reactivity has been developed across a wide spectrum of substrates: alkenes,[11b,d,12] alkynes,[13] enol ethers,[14] furans,[15] indoles,[16] and even arene moieties.[17] There have also been some unique

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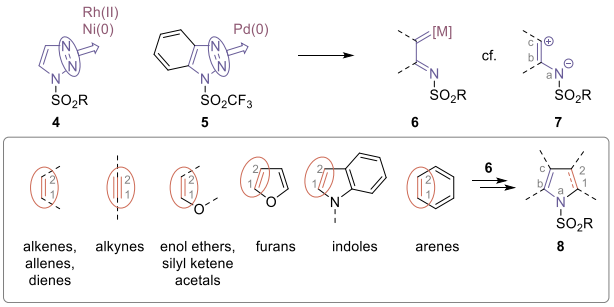
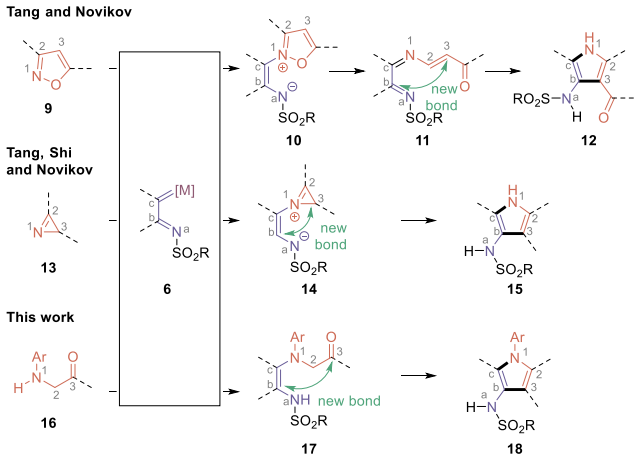
Scheme 1. General Reactivity of 1-Sufonyl-1,2,3-triazoles and Selected Application to the Synthesis of Pyrroles and Indoles



approaches to pyrroles and indoles from unsaturated carbonyl species,[18] alcoholic unsaturated carbonyl species,[19] unsaturated 1-STs,[20] and vinyl anilines.[21] The versatility of 1-ST reactivity means that many reactions are possible that result in heterocycle formation by the inclusion of a nitrogen-containing tether[22,23] or by providing valuable access to substrates that can be converted into five-membered azaheterocycles in short order.[24,25] In the majority of these examples, the mechanism dictates that the nitrogen atom remaining following denitrogenation of the triazole becomes the heteroatom component of the heterocycle that is generated. However, in reactions of 1-STs with certain nitrogen-containing substrates, the triazole nitrogen can become a 3-aza substituent of the pyrrole (Scheme 2).

Scheme 2. Approaches to 3-Azapyrroles from 1-Sufonyl-1,2,3-triazoles and This Approach



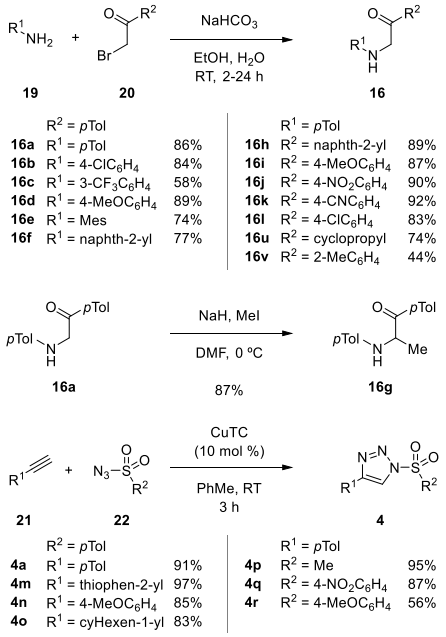
Upon treatment with a Rh(II) carboxylate, 1-STs formed an electron-deficient metallocarbene **6** that reacted with the nitrogen lone pair of isoxazoles **10**. Ring opening of the isoxazole **11** was followed by cyclization to form a pyrrole **12** with a 3-azasulfonyl substituent.[26] In a similar fashion but with azirenes, the azirene **13** lone pair reacted with the highly electron-deficient rhodium carbene **6** followed by collapse of the intermediate to form a pyrrole **15**, again with a 3-azasulfonyl substituent.[27]

The insertion of metallocarbenes into X−H bonds has been developed into a valuable reaction,[28] and this formation of C−N bonds from N−H bonds is another class of transformation that has been demonstrated with 1-STs.[21,29] Here, we recognized that α-aminoketones are the hydrated equivalent of azirenes. Therefore, bringing together an α-aminoketone **16** and a 1-ST through N−H bond insertion (**17**) and then performing cyclodehydration would result in a strategically complementary approach to valuable 3-azapyrroles **18**.

RESULTS

The substrates for this study, namely, α-aminoketones and 1-STs are both readily accessed from readily available materials (Scheme 3). The α-aminoketones **16** were formed by simple

Scheme 3. Synthesis of α-Aminoketones 16 and 1-STs 4 Used in This Work



	R^2 = *p*Tol			R^1 = *p*Tol	
16a	R^1 = *p*Tol	86%	**16h**	R^2 = naphth-2-yl	89%
16b	R^1 = 4-ClC$_6$H$_4$	84%	**16i**	R^2 = 4-MeOC$_6$H$_4$	87%
16c	R^1 = 3-CF$_3$C$_6$H$_4$	58%	**16j**	R^2 = 4-NO$_2$C$_6$H$_4$	90%
16d	R^1 = 4-MeOC$_6$H$_4$	89%	**16k**	R^2 = 4-CNC$_6$H$_4$	92%
16e	R^1 = Mes	74%	**16l**	R^2 = 4-ClC$_6$H$_4$	83%
16f	R^1 = naphth-2-yl	77%	**16u**	R^2 = cyclopropyl	74%
			16v	R^2 = 2-MeC$_6$H$_4$	44%

	R^2 = *p*Tol			R^1 = *p*Tol	
4a	R^1 = *p*Tol	91%	**4p**	R^2 = Me	95%
4m	R^1 = thiophen-2-yl	97%	**4q**	R^2 = 4-NO$_2$C$_6$H$_4$	87%
4n	R^1 = 4-MeOC$_6$H$_4$	85%	**4r**	R^2 = 4-MeOC$_6$H$_4$	56%
4o	R^1 = cyHexen-1-yl	83%			

S_N2 displacement of commercial α-haloketones **20** by anilines **19**. Additional substitution could be introduced to the α-position of the ketone owing to its acidic nature (**16g**). The 1-STs **4** were formed in excellent yield by copper-catalyzed azide−alkyne cycloaddition (CuAAC), and the modular nature of 1-ST synthesis is a key strength to this methodology. It is noteworthy that the use of copper(I) thiophene-2-carboxylate (CuTC) has been specifically developed for 1-ST synthesis.[9]

Next, the focus was establishing the optimum conditions for insertion of the metallocarbene derived from the 1-ST into the N−H bond of an appropriate aniline to bring together all the requisite atoms for the planned pyrrole synthesis (Table 1). A 4-tolyl-1-tosyltriazole **4a** was treated with a slight excess of α-aminoketone **16a** and 5 mol % of $Rh_2(OAc)_4$ in toluene at 80 °C with 4 Å molecular sieves.[30] These conditions resulted in the formation of the N−H insertion product **17a** in high yield (81%, entry 1).[31] Commonly employed Rh_2(octanoate)$_4$ and $Rh_2(esp)_2$[32] also promoted the N−H bond insertion but with lower efficiency, whereas no reaction occurred with bulky catalysts Rh_2(triphenylacetate)$_4$ and Rh_2(*S*-*t*PTTL)$_4$[33] (entries 4 and 5). The choice of solvent had a minor effect on the reaction outcome, but the yield was improved to 93% when using toluene (entries 6−8). Increasing the temperature from 60 to 80 °C provided a small increase in yield (entry 9), but increasing the temperature further caused the yield to decrease (entries 10 and 11); no reaction occurred below 60 °C (entry 12). These findings were congruous with previous work that

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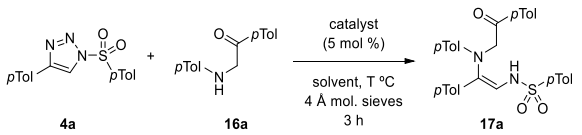
Table 1. Optimization of N−H Insertion[a]



4a 16a 17a

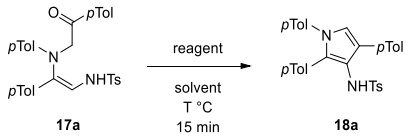
entry	catalyst	solvent	T (°C)	yield (%)
1	$Rh_2(OAc)_4$	$CHCl_3$	60	81
2	$Rh_2(esp)_2$	$CHCl_3$	60	70
3	$Rh_2(octanoate)_4$	$CHCl_3$	60	38
4	$Rh_2(TPA)_4$	$CHCl_3$	60	no reaction
5	$Rh_2(S\text{-}t\text{PTTL})_4$	$CHCl_3$	60	no reaction
6	$Rh_2(OAc)_4$	$(CH_2Cl)_2$	60	87
7	$Rh_2(OAc)_4$	CH_2Cl_2	60	91
8	$Rh_2(OAc)_4$	PhMe	60	93
9	**$Rh_2(OAc)_4$**	**PhMe**	**80**	**94**
10	$Rh_2(OAc)_4$	PhMe	100	85
11	$Rh_2(OAc)_4$	PhMe	120	58
12	$Rh_2(OAc)_4$	PhMe	40	no reaction

[a]0.2 mmol **4a**, 1.1 equiv of **16a**, 0.03 M, sealed vial, yield by internal standard ^{1}H NMR.

showed $Rh_2(OAc)_4$ and $Rh_2(octanoate)_4$ to be the most effective for related N−H bond insertions of α-amino esters, carbamates, and carbazoles.[21,29] However, this process was more tolerant to solvent compared with other processes, specifically with toluene being generally incompatible in the other examples.

It was anticipated that the Lewis acidic nature of the Rh(II) carboxylate might also promote cyclodehydration of the 1,2-diaminoalkene to form the corresponding pyrrole, but this transformation was not detected. Therefore, the heterocycle forming process was evaluated in a separate[23d,26b,34] operation (Table 2).

Table 2. Optimization of Cyclodehydration[a]



17a 18a

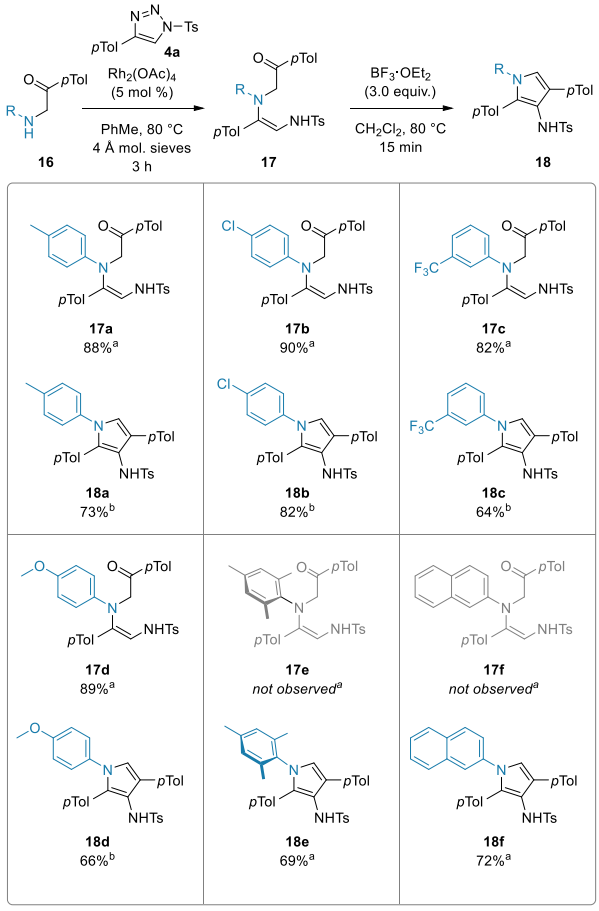
entry	reagent (equiv)	solvent	T (°C)	yield (%)
1	$BF_3{\cdot}OEt_2$ (0.5)	CH_2Cl_2	80	49
2	$BF_3{\cdot}OEt_2$ (1.0)	CH_2Cl_2	80	66
3	**$BF_3{\cdot}OEt_2$ (3.0)**	**CH_2Cl_2**	**80**	**72**
4	$BF_3{\cdot}OEt_2$ (3.0)	$(CH_2Cl)_2$	80	65
5	$BF_3{\cdot}OEt_2$ (3.0)	PhMe	80	19
6	$BF_3{\cdot}OEt_2$ (3.0)	MeCN	80	38
7	$BF_3{\cdot}OEt_2$ (3.0)	CH_2Cl_2	60	32
8	$BF_3{\cdot}OEt_2$ (3.0)	CH_2Cl_2	40	32

[a]0.2 mmol **17a**, 0.03 M, sealed vial, yield by internal standard ^{1}H NMR.

Treatment of the 1,2-diaminoalkene **17a** with a selection of dehydrating/acidic reagents; including *p*-toluene sulfonic acid, trimethylsilyl triflate, acetic acid, and phosphorus oxychloride resulted in the decomposition of substrate with only a minimal amount of the desired pyrrole **18a**. Gratifyingly, using $BF_3{\cdot}OEt_2$[35] (0.5 equiv) in dichloromethane at 80 °C gave a modest 49% yield of pyrrole **18a** (Table 2, entry 1) with a cleaner reaction profile (^{1}H NMR). Increasing the amount of Lewis acid from 0.5 to 3.0 equiv was accompanied by an increase in yield to 72% (entries 2 and 3). 1,2-Dichloroethane, toluene, and acetonitrile were considered as alternative solvents, but the yields were lower than those of dichloromethane, giving complex mixtures (entries 4−6). Reducing the temperature to less than 80 °C resulted in a more sluggish reaction (entries 7 and 8).

With the reaction conditions for a pyrrole synthesis sequence established, the generality of this process was explored (Scheme 4). Upon varying the *N*-aryl substituent,

Scheme 4. Scope of Arylamine in the Pyrrole Synthesis



[a]Isolated yield from Rh(II)-catalyzed N−H insertion. [b]Isolated yield from $BF_3{\cdot}OEt_2$-promoted cyclodehydration.

the Rh(II)-catalyzed N−H insertion and $BF_3{\cdot}OEt_2$ promoted cyclodehydration were found to be highly tolerant with good to excellent yields obtained for both reactions (**17a−d** and **18a−d**). Surprisingly, when a mesityl group or naphthyl group was used, the Rh(II)-catalyzed reaction led to the pyrroles **18e,f** in good yield directly, and no 1,2-diamine product **17e,f** was observed. This difference in reactivity was attributed to promotion of the cyclization by raising the energy of unreactive conformations through steric interactions, placing the reacting centers in close proximity. Aliphatic amines were challenging substrates for the Rh(II)-catalyzed reaction and so were not compatible with this process, presumably owing to their increased basicity.

Variation of the ketone substituent was also studied, allowing control of the 4- and 5-positions of the resulting pyrrole (Scheme 5). Having an additional α-substituent in the substrate aminoketone was evaluated, and this proved to be

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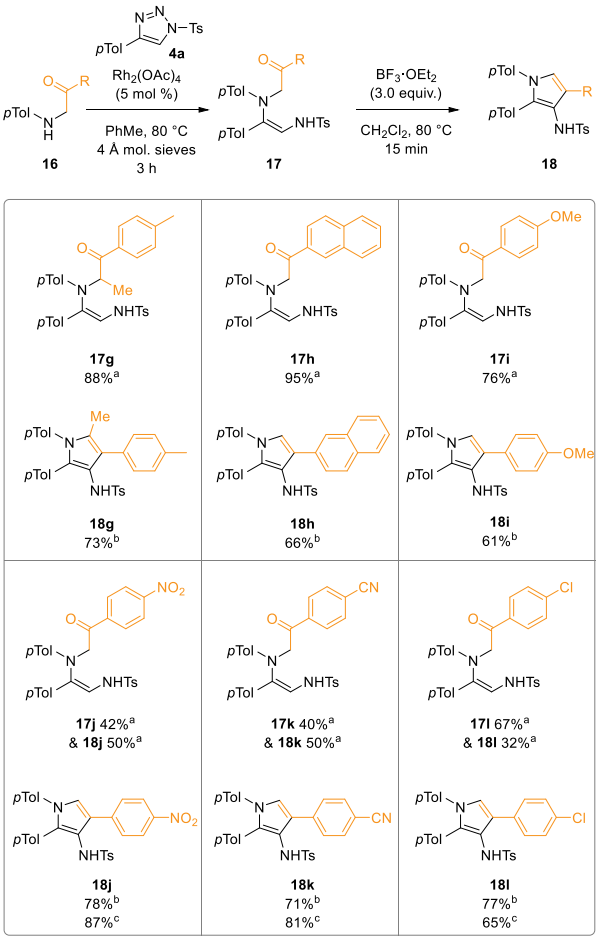
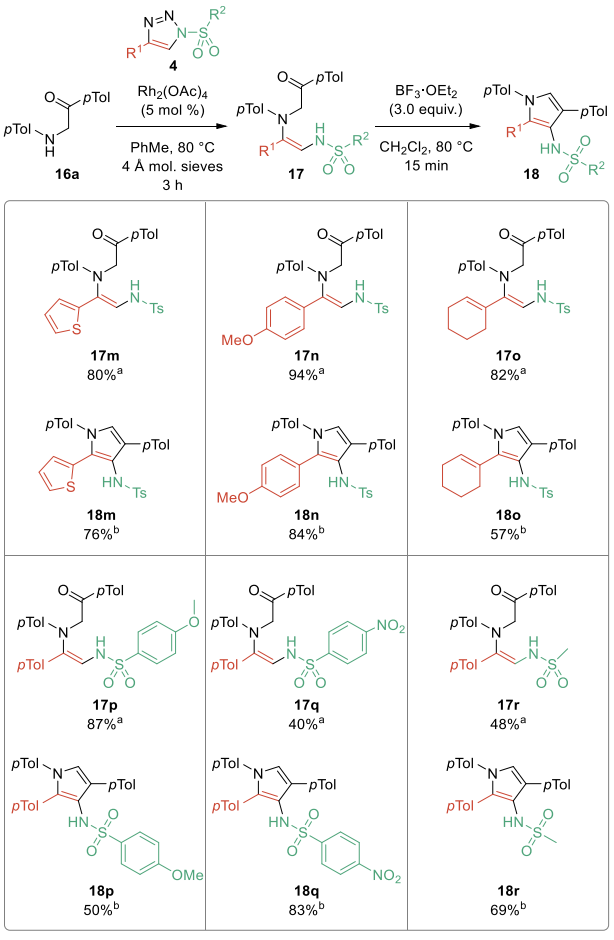
Scheme 5. Scope of Ketone in the Pyrrole Synthesis



[a]Isolated yield from Rh(II)-catalyzed N−H insertion. [b]Isolated yield from $BF_3{\cdot}OEt_2$-promoted cyclodehydration. [c]Isolated yield from Rh(II)-catalyzed N−H insertion with 16 h reaction time.

Scheme 6. Scope of 1-ST in the Pyrrole Synthesis



[a]Isolated yield from Rh(II)-catalyzed N−H insertion. [b]Isolated yield from $BF_3{\cdot}OEt_2$-promoted cyclodehydration.

compatible with the optimized conditions, giving a fully substituted pyrrole product **18g** in high yield over the two operations.

When more conjugated or electron-rich ketone substituents were studied, these also gave good yields for the two operations (**18h,i**). Interestingly, using more electron-withdrawing substituents NO_2, CN, and Cl gave the expected N−H insertion products **17j−l** alongside the corresponding pyrroles **18j−l**, giving almost quantitative combined yields of the products. The two products were readily separated by column chromatography, and the 1,2-diaminoalkenes **17j−l** could be transformed into their corresponding pyrroles **18j−l** in good yield. Extending the reaction time in the presence of rhodium catalyst to 16 h led to formation of only the pyrrole products in high yield (87% of **18j**, 81% of **18k**, and 65% of **18l**). It is suggested that direct formation of pyrroles proceeded in these cases via the same products of N−H insertion, but that the more electron-withdrawing substituents activated the ketone toward nucleophilic attack, allowing cyclodehydration to occur with the more mildly Lewis acidic Rh(II) catalyst. This is consistent with the more electron-withdrawing NO_2 and CN groups giving more pyrrole product than the Cl substituent.

Different substituents at the 4-position of 1-ST **4** were also studied (Scheme 6). Heteroaromatic, electron-rich aromatic, and alkenyl 1-ST 4-substituents gave excellent yields for N−H insertion (**17m−o**). Interestingly, the alkene substrate completed N−H insertion (**17o**), despite the known intramolecular rearrangement of alkenyl 1-STs to a different class of pyrrole.[20] Pyrroles **18m,n** were formed from these products using $BF_3{\cdot}OEt_2$, again all with good to excellent yield. Variation of the sulfonyl group was also examined. Use of an electron-donating *p*-$MeOC_6H_4SO_2$ group gave an excellent yield for N−H insertion (**17p**) but a moderate yield for cyclization to pyrrole **18p**. On the other hand, the electron-withdrawing *p*-$NO_2C_6H_4SO_2$ group and the small mesyl group gave a moderate yield for N−H insertion for **17q,r** but an excellent yield for cyclodehydration to the pyrrole **18q,r**.

The key contributors to inefficiency in synthesis often come not from the reactions themselves but in the purification of intermediates, so combining or telescoping multiple operations in one pot or domino sequences is an excellent way to boost efficiency.[36] CuAAC is highly versatile and has been incorporated in one-pot sequences with rhodium(II) reactions of 1-STs since the earliest work in the field,[18c,20,37] so this was also investigated here (Scheme 7). Although, each of the sequential operations (CuAAC, N−H insertion, and cyclodehydration) had reagents and catalysts that should be tolerant to the previous conditions in the sequence, their solvent varied. Dichloromethane was selected for the one-pot process because it was significantly better than other solvents in the

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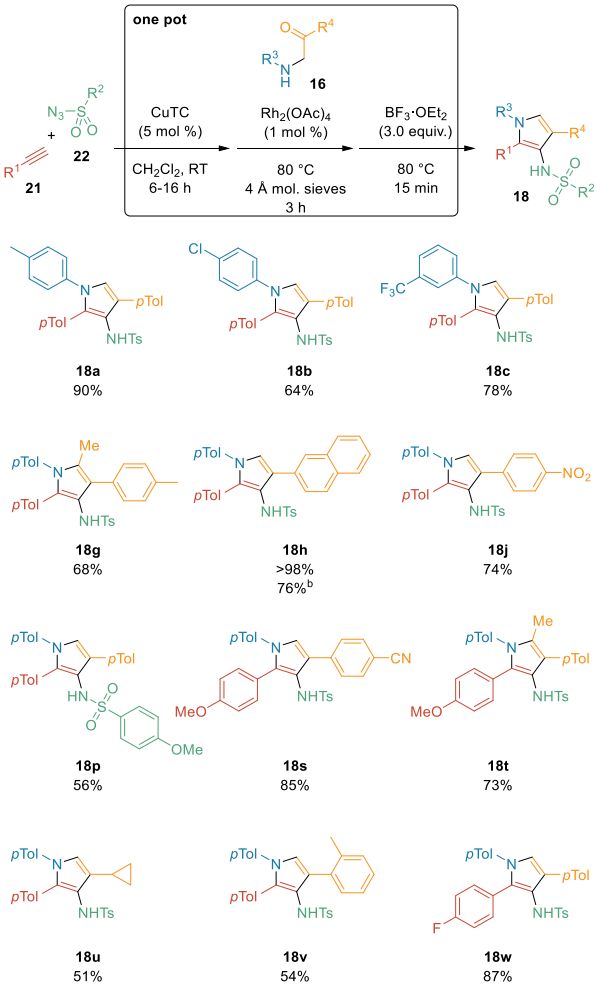
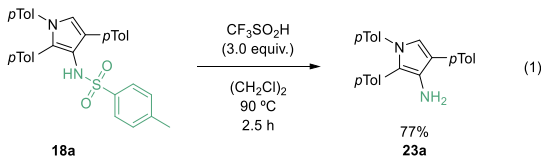
Scheme 7. Three-Step, One-Pot Synthesis of Pyrroles 18 from Alkynes 21, Sulfonyl Azides 22, and α-Aminoketones 16[a]



[a]Isolated yield. [b]On 4.6 mmol scale, using $(CH_2Cl)_2$ in place of CH_2Cl_2, isolated yield.

cyclodehydration step and worked well with the other steps, and the amount was selected to match the concentration of the most sensitive Rh(II)-catalyzed step. Treatment of *p*-tolylacetylene with tosyl azide in the presence of CuTC in CH_2Cl_2 gave complete conversion to the corresponding 1-ST **4a**. Without isolation, α-aminoketone **16a** and $Rh_2(OAc)_4$ were added to the mixture, and the vial was sealed and heated for 3 h at 80 °C. Then $BF_3{\cdot}OEt_2$ (3.0 equiv) was added, and the reaction mixture was stirred for a further 15 min at 80 °C. Standard aqueous workup ($NaHCO_3$) and filtration through silica gel afforded the pyrrole **18a** in 90% yield. This represented a marked improvement over the three separate steps (90 vs 58%) as well as making the overall process much more time- and material-efficient. Furthermore, the amount of copper and rhodium catalysts used was decreased to 5 and 1 mol %, respectively, without any deleterious effect. The one-pot process was applied to a range of terminal alkynes **21**, sulfonyl azides **22**, and amines **16**, all of which gave excellent yields of the corresponding pyrroles **18** with considerable improvement over the stepwise equivalent. The one-pot procedure was also completed on a larger scale (4.61 mmol), using $(CH_2Cl)_2$ in place of CH_2Cl_2 and under reflux instead of in a sealed vial, and the protocol delivered the product **18h** in excellent 76% yield.

Finally, the cleavage of the *N*-sulfonyl bond was demonstrated (eq 1). The *N*-tosyl pyrrole **18a** was treated with triflic acid at 90 °C, followed by workup with ethylene diamine,[38] to reveal the pyrrole with a NH_2 group **23a** in 77% yield.



CONCLUSION

A procedure has been developed that allows rapid assembly of 3-azapyrroles from readily available starting materials. The 1-ST and secondary amine starting materials were accessed in high yield from readily available building blocks. Rhodium(II) acetate was the optimum catalyst to promote 1-ST denitrogenation and insertion into the N−H bond of a range of α-aminoketones to form 1,2-aminoalkenes in high yields. For bulky arylamines and electron-deficient ketones, the 1,2-aminoalkenes cyclized into the corresponding 3-azapyrroles under rhodium catalysis, but for most examples, this was not the case and $BF_3{\cdot}OEt_2$ proved to be a reliable Lewis acid for promoting the transformation into the heterocyclic products. These steps could be conducted individually or telescoped into a one-pot process beginning from sulfonyl azides, alkynes, and ketones, exploiting the orthogonal reactivity in the sequence. The availability of individual substrates means that this method represents a highly modular approach to pyrroles, allowing each of the five substituents to be customized through judicious choice of starting materials.

EXPERIMENTAL DETAILS

CAUTION: Nitrogen-rich compounds, such as azides and triazoles, can decompose violently with the loss of nitrogen gas. Although no problems were encountered in this study, appropriate precautions should be taken.

General Information and Methods. NMR spectra were recorded on 400 and 500 MHz Bruker spectrometers. Chemical shifts are given in parts per million, and the spectra are calibrated to the residual ^1H and ^{13}C signals of the solvents. ^{13}C NMR spectra were collected with complete proton decoupling, and assignments were made using COSY, HSQC, HMBC, and NOESY experiments. Samples were melted directly from the procedures described. High-resolution mass spectra were obtained on Agilent 6546 LC/Q-TOF and Bruker microTOFq instruments by Analytical Services at the University of Glasgow School of Chemistry. IR spectra were recorded using spectrometers fitted with an ATR device. CH_2Cl_2 and toluene were purified on a PureSolv PM500, and other reagents were used as received. Reactions were monitored by thin layer chromatography (TLC) using Merck TLC silica gel 60 F254 aluminum-foil baked plates. Compounds were visualized by UV light at nanometer resolution or by staining with potassium permanganate. Column chromatography was performed using a Teledyne ISCO Combiflash Rf+ system using Redisep Rf silica cartridges.

General Procedure 1: CuAAC to Form 1STs. Copper(I) thiophene-2-carboxylate (10 mol %) and alkyne **21** (1.1 equiv) were dissolved in PhMe (0.1 M) and cooled to 0 °C (ice bath). After 10 min, sulfonyl azide **22** (1.0 equiv) was added in one portion and the reaction mixture was allowed to reach ambient temperature. When the reaction was complete (TLC, 1−3 h), the mixture was diluted with saturated aqueous NH_4Cl and extracted with ethyl acetate (3 × 10 mL $mmol^{-1}$). The combined organic layers were washed with

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brine, dried ($MgSO_4$), filtered, and concentrated in vacuo. The residue was purified by flash column chromatography (SiO_2, rapid gradient of 10−30% ethyl acetate in petroleum ether) to give the 1-ST **4**.

*4-(4-Tolyl)-1-tosyl-1,2,3-triazole (**4a**).* 4-Ethynyltoluene (547 μL, 4.3 mmol, 1.1 equiv) and 4-toluenesulfonyl azide (809 mg, 4.1 mmol, 1.0 equiv) were treated with CuTC (69 mg, 0.36 mmol, 9 mol %) in PhMe (40 mL) according to General Procedure 1 to give the title compound **4a** (1.17 g, 91%) as a white solid: mp 127 °C dec (lit. 158−159 °C);[39] ν_{max} (film) 3150, 2940, 1593, 1497, 1392, 1194, and 1179 cm^{-1}; ^1H NMR (400 MHz, 25.0 °C, $CDCl_3$) δ 8.26 (1 H, s, triazole CH), 8.02 (2 H, d, J = 8.4 Hz, Ar), 7.71 (2 H, d, J = 8.4 Hz, Ar), 7.39 (2 H, d, J = 7.8 Hz, Ar), 7.23 (2 H, d, J = 7.8 Hz, Ar), 2.45 (3 H, s, CH_3) and 2.38 (3 H, s, CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, 25.0 °C, $CDCl_3$) δ 147.4 (Ar), 147.3 (triazole C4), 139.1 (Ar), 133.2 (Ar), 130.4 (2 × ArH), 129.7 (2 × ArH), 128.7 (2 × ArH), 126.0 (Ar), 126.0 (2 × ArH), 118.5 (triazole C5), 21.8 (CH_3) and 21.3 (CH_3); HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{16}H_{15}N_3NaO_2S^+$ 336.0777; found 336.0767. Recorded data are consistent with previous values.[39]

*4-(Thiophen-2-yl)-1-tosyl-1,2,3-triazole (**4m**).* 2-Ethynylthiophene (438 μL, 4.6 mmol, 1.1 equiv) and 4-toluenesulfonyl azide (828 mg, 4.2 mmol, 1.0 equiv) were treated with CuTC (80 mg, 0.42 mmol, 10 mol %) in PhMe (42 mL) according to General Procedure 1 to give the title compound **4m** (1.24 g, 97%) as a white solid: mp 87 °C dec (lit. 140−141 °C);[18f] ν_{max} (film) 3136, 2924, 1593, 1393, 1346, 1196, 1177, and 1092 cm^{-1}; ^1H NMR (400 MHz, 25.0 °C, $CDCl_3$) δ 8.20 (1 H, s, triazole CH), 8.02 (2 H, d, J = 8.5 Hz, Ar), 7.44 (1 H, dd, J = 3.6, 1.2 Hz, thiophene CH), 7.39 (2 H, d, J = 8.5 Hz, Ar), 7.34 (1 H, dd, J = 5.1, 1.2 Hz, thiophene CH), 7.08 (1 H, dd, J = 5.1, 3.6 Hz, thiophene CH) and 2.45 (3 H, s, CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, 25.0 °C, $CDCl_3$) δ 147.4 (triazole C4), 142.5 (thiophene C2), 133.0 (Ar), 130.8 (Ar), 130.5 (2 × ArH), 128.7 (2 × ArH), 127.8 (thiophene CH), 126.3 (thiophene CH), 125.6 (thiophene CH), 118.1 (triazole C5) and 21.8 (CH_3); HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{13}H_{11}N_3NaO_2S_2^+$ 328.0185; found 328.0184. Recorded data are consistent with previous values.[18f]

*4-(4-Methoxyphenyl)-1-tosyl-1,2,3-triazole (**4n**).* 1-Ethynyl-4-methoxybenzene (535 μL, 4.1 mmol, 1.1 equiv) and 4-toluenesulfonyl azide (740 mg, 3.8 mmol, 1.0 equiv) were treated with CuTC (71 mg, 0.37 mmol, 10 mol %) in PhMe (40 mL) according to General Procedure 1 to give the title compound **4n** (1.05 g, 85%) as a white solid: mp 96 °C dec (lit. 100−101 °C);[40] ν_{max} (film) 3144, 2932, 2839, 1616, 1497, 1393, 1331, 1250, 1177, and 1088 cm^{-1}; ^1H NMR (400 MHz, 25.0 °C, $CDCl_3$) δ 8.22 (1 H, s, triazole CH), 8.01 (2 H, d, J = 8.5 Hz, Ar), 7.74 (2 H, d, J = 8.9 Hz, Ar), 7.37 (2 H, d, J = 8.5 Hz, Ar), 6.95 (2 H, d, J = 8.9 Hz, Ar), 3.83 (3 H, s, OCH_3) and 2.43 (3 H, s, CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, 25.0 °C, $CDCl_3$) δ 160.2 (Ar), 147.3 (Ar), 147.2 (triazole C4), 133.1 (Ar), 130.4 (2 × ArH), 128.6 (2 × ArH), 127.4 (2 × ArH), 121.4 (Ar), 117.9 (triazole C5), 114.4 (2 × ArH), 55.3 (OCH_3) and 21.8 (CH_3); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{16}H_{16}N_3O_3S^+$ 330.0907; found 330.0909. Recorded data are consistent with previous values.[40]

*4-(Cyclohexen-1-yl)-1-tosyl-1,2,3-triazole (**4o**).* 1-Ethynylcyclohex-1-ene (485 μL, 4.1 mmol, 1.1 equiv) and 4-toluenesulfonyl azide (740 mg, 3.8 mmol, 1.0 equiv) were treated with CuTC (71 mg, 0.37 mmol, 10 mol %) in PhMe (40 mL) according to General Procedure 1 to give the title compound **4o** (950 mg, 83%) as a white solid: mp 100 °C dec (lit. 102−103 °C);[39] ν_{max} (film) 3148, 2928, 2859, 1593, 1389, 1177, and 1092 cm^{-1}; ^1H NMR (400 MHz, 25.0 °C, $CDCl_3$) δ 7.97 (2 H, d, J = 8.5 Hz, Ar), 7.88 (1 H, s, triazole CH), 7.36 (2 H, d, J = 8.5 Hz, Ar), 6.66 (1 H, tt, J = 3.9, 1.8 Hz, =CH), 2.43 (3 H, s, CH_3), 2.34−2.27 (2 H, m, CH_2), 2.22−2.15 (2 H, m, CH_2), 1.78−1.71 (2 H, m, CH_2) and 1.70−1.61 (2 H, m, CH_2); $^{13}C\{^1H\}$ NMR (101 MHz, 25.0 °C, $CDCl_3$) δ 148.9 (triazole C4), 147.0 (Ar), 133.3 (Ar), 130.3 (2 × ArH), 128.5 (2 × ArH), 127.7 (=CH), 125.8 (=C), 117.3 (triazole C5), 26.2 (CH_2), 25.3 (CH_2), 22.2 (CH_2), 22.0 (CH_2) and 21.8 (CH_3); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{15}H_{18}N_3O_2S^+$ 304.1114; found 304.1113. Recorded data are consistent with previous values.[39]

*1-Methanesulfonyl-4-(4-tolyl)-1,2,3-triazole (**4p**).* 4-Ethynyltoluene (558 μL, 4.4 mmol, 1.1 equiv) and methanesulfonyl azide (484 mg, 4.0 mmol, 1.0 equiv) were treated with CuTC (76 mg, 0.40 mmol, 10 mol %) in PhMe (40 mL) according to General Procedure 1 to give the title compound **4p** (898 mg, 95%) as a white solid: mp 95 °C dec (lit. 120−122 °C dec.);[41] ν_{max} (film) 3140, 3028, 2924, 1381, 1231, 1184, 1161, and 1038 cm^{-1}; ^1H NMR (500 MHz, 25.0 °C, $CDCl_3$) δ 8.26 (1 H, s, triazole CH), 7.76 (2 H, d, J = 8.0 Hz, Ar), 7.28 (2 H, d, J = 8.0 Hz, Ar), 3.56 (3 H, s, CH_3) and 2.41 (3 H, s, CH_3); $^{13}C\{^1H\}$ NMR (126 MHz, 25.0 °C, $CDCl_3$) δ 147.6 (triazole C4), 139.4 (Ar), 129.8 (2 × ArH), 126.1 (2 × ArH), 125.8 (Ar), 118.4 (triazole C5), 42.7 (CH_3) and 21.4 (CH_3); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{10}H_{12}N_3O_2S^+$ 238.0645; found 238.0646. Recorded data are consistent with previous values.[41]

*1-(4-Nitrobenzenesulfonyl)-4-(4-tolyl)-1,2,3-triazole (**4q**).* 4-Ethynyltoluene (533 μL, 4.2 mmol, 1.1 equiv) and 4-nitrobenzenesulfonyl azide (913 mg, 4.0 mmol, 1.0 equiv) were treated with CuTC (76 mg, 0.40 mmol, 10 mol %) in PhMe (40 mL) according to General Procedure 1 to give the title compound **4q** (1.20 g, 87%) as a white solid: mp 106 °C dec; ν_{max} (film) 3140, 3109, 1532, 1408, 1397, 1346, and 1188 cm^{-1}; ^1H NMR (500 MHz, 25.0 °C, $CDCl_3$) δ 8.44 (2 H, d, J = 9.0 Hz, Ar), 8.36 (2 H, d, J = 9.0 Hz, Ar), 8.30 (1 H, s, triazole CH), 7.71 (2 H, d, J = 8.2 Hz, Ar), 7.25 (2 H, d, J = 8.2 Hz, Ar) and 2.39 (3 H, s, CH_3); $^{13}C\{^1H\}$ NMR (126 MHz, 25.0 °C, $CDCl_3$) δ 151.6 (Ar), 148.0 (triazole C4), 141.6 (Ar), 139.6 (Ar), 130.1 (2 × ArH), 129.8 (2 × ArH), 126.1 (2 × ArH), 125.4 (Ar), 125.0 (2 × ArH), 118.6 (triazole C5) and 21.4 (CH_3); HRMS (ESI-TOF) m/z $[M(hydrolyzed\ triazole) + H]^+$ calcd for $C_9H_{10}N_3^+$ 160.0869; found 160.0875.

*1-(4-Methoxylphenylsulfonyl)-4-(4-tolyl)-1,2,3-triazole (**4r**).* 4-Ethynyltoluene (279 μL, 2.2 mmol, 1.1 equiv) and 4-methoxybenzenesulfonyl azide (426 mg, 2.0 mmol, 1.0 equiv) were treated with CuTC (38 mg, 0.20 mmol, 10 mol %) in PhMe (20 mL) according to General Procedure 1 to give the title compound **4r** (372 mg, 56%) as a white solid: mp 102 °C dec; ν_{max} (film) 2940, 2923, 1593, 1577, 1497, 1391, 1233, and 1168 cm^{-1}; ^1H NMR (500 MHz, 25.0 °C, $CDCl_3$) δ 8.26 (1 H, s, triazole CH), 8.08 (2 H, d, J = 9.1 Hz, Ar), 7.71 (2 H, d, J = 8.1 Hz, Ar), 7.24 (2 H, d, J = 8.1 Hz, Ar), 7.03 (2 H, d, J = 9.1 Hz, Ar), 3.89 (3 H, s, OCH_3) and 2.38 (3 H, s, CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, 25.0 °C, $CDCl_3$) δ 12707.0 (Ar), 165.3 (Ar), 147.4 (triazole C4), 139.1 (Ar), 131.2 (2 × ArH), 129.7 (2 × ArH), 127.9 (Ar), 126.0 (2 × ArH), 118.4 (triazole C5), 115.1 (2 × ArH), 55.9 (OCH_3) and 21.3 (CH_3); HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{16}H_{15}N_3NaO_3S^+$ 352.0726; found 352.0719. Recorded data are consistent with previous values.[42]

General Procedure 2: Formation of α-Aminoketones. Amine **19** (1.0 equiv) was dissolved in a 1:1 mixture of water and ethanol (0.2 M). $NaHCO_3$ (1.0 equiv) was added followed by the α-bromoketone **20** (1.0 equiv), and the reaction mixture was stirred until completion (TLC, 2−24 h). The reaction mixture was diluted with ethyl acetate, and the aqueous phase was extracted with ethyl acetate (3 × 5 mL $mmol^{-1}$). The combined organic layers were washed with brine, dried ($MgSO_4$), and concentrated in vacuo. This product was either purified by recrystallization from $CHCl_3$/pentane or by column chromatography (SiO_2, gradient of 10−30% EtOAc in petroleum ether).

*1-(4-Tolyl)-2-(4-tolylamino)ethan-1-one (**16a**).* *p*-Toluidine (1.00 g, 9.4 mmol, 1.0 equiv) and 2-bromo-4′-methylacetophenone (2.00 g, 9.4 mmol, 1.0 equiv) were treated with sodium hydrogen carbonate (789 mg, 9.4 mmol, 1.0 equiv) in ethanol (30 mL) and water (30 mL) according to General Procedure 2 for 16 h, and then the crude product was purified by recrystallization ($CHCl_3$/pentane) to give the title compound **16a** (1.93 g, 86%) as a yellow solid: mp 130−138 °C (lit. 130−133 °C);[43] ν_{max} (film) 3405, 3029, 1682, 1612, 1527, and 1356 cm^{-1}; ^1H NMR (500 MHz, 22.2 °C, $CDCl_3$) δ 7.92 (2 H, d, J = 8.5 Hz, Ar), 7.31 (2 H, d, J = 7.8 Hz, Ar), 7.04 (2 H, d, J = 7.8 Hz, Ar), 6.65 (2 H, d, J = 8.5 Hz, Ar), 4.85 (1 H, br s, NH), 4.58 (2 H, s, CH_2), 2.44 (3 H, s, CH_3) and 2.26 (3 H, s, CH_3); $^{13}C\{^1H\}$ NMR (126 MHz, 22.6 °C, $CDCl_3$) δ 194.9 (C═O), 144.9 (Ar), 144.8 (Ar), 132.5 (Ar), 129.8 (2 × ArH), 129.5 (2 × ArH), 127.8 (2 × ArH),

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127.0 (Ar), 113.2 (2 × ArH), 50.6 (CH_2), 21.8 (CH_3) and 20.4 (CH_3); HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{16}H_{17}NNaO^+$ 262.1202; found 262.1204.

*2-(4-Chlorophenylamino)-1-(4-tolyl)ethan-1-one (**16b**).* 4-Chloroaniline (255 mg, 2.0 mmol, 1.0 equiv) and 2-bromo-4′-methylacetophenone (426 mg, 2.0 mmol, 1.0 equiv) were treated with sodium hydrogen carbonate (168 mg, 2.0 mmol, 1.0 equiv) in ethanol (5 mL) and water (5 mL) according to General Procedure 2 for 24 h, and then the crude product was purified by recrystallization ($CHCl_3$/pentane) to give the title compound **16b** (438 mg, 84%) as a white solid: mp 125 °C dec (lit. 167−169 °C);[44] ν_{max} (film) 3393, 3030, 1675, 1603, 1499, 1353, 1188, and 1092 cm^{-1}; ^1H NMR (400 MHz, 22.4 °C, $CDCl_3$) δ 7.90 (2 H, d, J = 8.2 Hz, Ar), 7.31 (2 H, d, J = 8.2 Hz, Ar), 7.16 (2 H, d, J = 8.8 Hz, Ar), 6.64 (2 H, d, J = 8.8 Hz, Ar), 4.54 (2 H, s, CH_2) and 2.44 (3 H, s, CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, 22.8 °C, $CDCl_3$) δ 194.2 (C═O), 145.6 (Ar), 145.0 (Ar), 132.2 (Ar), 129.6 (2 × ArH), 129.2 (2 × ArH), 127.8 (2 × ArH), 122.4 (Ar), 114.1 (2 × ArH), 50.1 (CH_2) and 21.7 (CH_3); HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{15}H_{14}ClNNaO^+$ 282.0656; found 282.0655.

*1-(4-Tolyl)-2-(3-trifluoromethylphenylamino)ethan-1-one (**16c**).* 3-Trifluoromethylaniline (323 mg, 2.0 mmol, 1.0 equiv) and 2-bromo-4′-methylacetophenone (426 mg, 2.0 mmol, 1.0 equiv) were treated with sodium hydrogen carbonate (168 mg, 2.0 mmol, 1.0 equiv) in ethanol (5 mL) and water (5 mL) according to General Procedure 2 for 16 h, and then the crude product was purified by recrystallization ($CHCl_3$/pentane) to give the title compound **16c** (343 mg, 58%) as a white solid: mp 133−135 °C; ν_{max} (film) 3402, 2928, 1678, 1605, 1501, 1362, 1339, 1254, 1161, and 1115 cm^{-1}; ^1H NMR (400 MHz, 25.0 °C, $CDCl_3$) δ 7.94 (2 H, d, J = 8.2 Hz, Ar), 7.33 (2 H, d, J = 8.2 Hz, Ar), 7.32−7.29 (1 H, m, Ar), 7.01−6.96 (1 H, m, Ar), 6.90−6.84 (2 H, m, Ar), 5.22 (1 H, br s, NH), 4.60 (2 H, s, CH_2) and 2.45 (3 H, s, CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, 25.0 °C, $CDCl_3$) δ 193.9 (C═O), 147.2 (Ar), 145.1 (Ar), 132.2 (Ar), 131.7 (q, J = 31.9 Hz, ArH), 129.7 (ArH), 129.6 (2 × ArH), 127.9 (2 × ArH), 124.3 (q, J = 272.3 Hz, CF_3), 116.3 (ArH), 114.1 (q, J = 4.1 Hz, ArH), 108.7 (q, J = 4.0 Hz, ArH), 49.7 (CH_2) and 21.8 (CH_3); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{16}H_{15}F_3NO^+$ 294.1100; found 294.1110.

*2-(4-Methoxyphenylamino)-1-(4-tolyl)ethan-1-one (**16d**).* *p*-Anisidine (246 mg, 2.0 mmol, 1.0 equiv) and 2-bromo-4′-methylacetophenone (426 mg, 2.0 mmol, 1.0 equiv) were treated with sodium hydrogen carbonate (168 mg, 2.0 mmol, 1.0 equiv) in ethanol (5 mL) and water (5 mL) according to General Procedure 2 for 24 h, and then the crude product was purified by recrystallization ($CHCl_3$/pentane) to give the title compound **16d** (454 mg, 89%) as a yellow solid: mp 97−100 °C (lit. 102−103 °C);[43] ν_{max} (film) 3395, 3007, 2930, 2832, 1675, 1607, 1515, 1236, 1182, and 1037 cm^{-1}; ^1H NMR (400 MHz, 22.4 °C, $CDCl_3$) δ 7.91 (2 H, d, J = 8.2 Hz, Ar), 7.31 (2 H, d, J = 8.2 Hz, Ar), 6.83 (2 H, d, J = 8.9 Hz, Ar), 6.68 (2 H, d, J = 8.9 Hz, Ar), 4.55 (2 H, s, CH_2), 3.76 (3 H, s, OCH_3) and 2.44 (3 H, s, CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, 23.0 °C, $CDCl_3$) δ 195.0 (C═O), 152.3 (Ar), 144.7 (Ar), 141.6 (Ar), 132.5 (Ar), 129.5 (2 × ArH), 127.8 (2 × ArH), 115.0 (2 × ArH), 114.2 (2 × ArH), 55.8 (OCH_3), 51.1 (CH_2) and 21.7 (CH_3); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{16}H_{18}NO_2^+$ 256.1332; found 256.1330.

*1-(4-Tolyl)-2-(2,4,6-trimethylphenylamino)ethan-1-one (**16e**).* 2,4,6-Trimethylaniline (271 mg, 2.0 mmol, 1.0 equiv) and 2-bromo-4′-methylacetophenone (426 mg, 2.0 mmol, 1.0 equiv) were treated with sodium hydrogen carbonate (168 mg, 2.0 mmol, 1.0 equiv) in ethanol (5 mL) and water (5 mL) according to General Procedure 2 for 16 h, and then the crude product was purified by recrystallization ($CHCl_3$/pentane) to give the title compound **16e** (397 mg, 74%) as an off white solid: mp 123 °C dec; ν_{max} (film) 3028, 2974, 2924, 2870, 1686, 1609, and 1069 cm^{-1}; ^1H NMR (400 MHz, 25.0 °C, $CDCl_3$) δ 7.84 (2 H, d, J = 7.8 Hz, Ar), 7.27 (2 H, d, J = 7.8 Hz, Ar), 6.84 (2 H, s, Ar), 4.54 (1 H, br s, NH), 4.48 (2 H, s, CH_2), 2.42 (3 H, s, CH_3), 2.35 (6 H, s, 2 × CH_3) and 2.24 (3 H, s, CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, 25.0 °C, $CDCl_3$) δ 196.4 (C═O), 144.6 (Ar), 143.9 (Ar), 132.5 (Ar), 131.1 (Ar), 129.5 (2 × ArH), 129.4 (2 × ArH), 129.0 (2 × Ar), 127.7 (2 × ArH), 55.3 (CH_2), 21.7 (CH_3), 20.5 (CH_3) and 18.7 (2 × CH_3); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{18}H_{22}NO^+$ 268.1696; found 268.1696.

*2-(Naphth-2-ylamino)-1-(4-tolyl)ethan-1-one (**16f**).* 2-Naphthylamine (285 mg, 2.0 mmol, 1.0 equiv) and 2-bromo-4′-methylacetophenone (426 mg, 2.0 mmol, 1.0 equiv) were treated with sodium hydrogen carbonate (202 mg, 2.4 mmol, 1.2 equiv) in ethanol (5 mL) and water (5 mL) according to General Procedure 2 for 16 h, and then the crude product was purified by recrystallization ($CHCl_3$/pentane) to give the title compound **16f** (422 mg, 77%) as a gray solid: mp 120−125 °C; ν_{max} (film) 3418, 3051, 2920, 1686, 1582, 1523, 1408, and 1235 cm^{-1}; ^1H NMR (400 MHz, 25.0 °C, $CDCl_3$) δ 8.09−8.04 (1 H, m, naphthyl CH), 7.99 (2 H, d, J = 8.1 Hz, Ar), 7.84−7.79 (1 H, m, naphthyl CH), 7.54−7.46 (2 H, m, naphthyl CH), 7.38 (1 H, dd, J = 8.2, 7.5 Hz, naphthyl CH), 7.34 (2 H, d, J = 8.1 Hz, Ar), 7.29−7.26 (1 H, m, naphthyl CH), 6.61 (1 H, dd, J = 7.5, 1.1 Hz, naphthyl CH), 5.83 (1 H, br s, NH), 4.73 (2 H, s, CH_2) and 2.46 (3 H, s, CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, 25.0 °C, $CDCl_3$) δ 194.6 (C═O), 145.0 (naphthyl C), 142.4 (Ar), 134.4 (naphthyl C), 132.5 (naphthyl C), 129.7 (2 × ArH), 128.6 (naphthyl CH), 128.0 (2 × ArH), 126.5 (naphthyl CH), 126.0 (naphthyl CH), 124.9 (naphthyl CH), 123.4 (Ar), 120.3 (naphthyl CH), 117.7 (naphthyl CH), 104.4 (naphthyl CH), 50.2 (CH_2) and 21.8 (CH_3); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{19}H_{18}NO^+$ 276.1383; found 276.1389.

*1-(4-Tolyl)-2-(4-tolylamino)propan-1-one (**16g**).* NaH (60% suspension in mineral oil, 50 mg, 1.25 mmol, 1.1 equiv) was suspended in DMF (10 mL) and cooled to 0 °C (ice bath), and 1-(4-tolyl)-2-(4-tolylamino)ethan-1-one **16a** (338 mg, 1.14 mmol, 1.0 equiv) was added in three portions. The reaction was stirred for 30 min and then MeI (92 μL, 1.48 mmol, 1.3 equiv) was added, and the reaction stirred for a further 3 h. Water was added, and the aqueous phase was extracted with Et_2O (3 × 15 mL). The combined organic layers were washed with water, brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. Purification by flash column chromatography (SiO_2, gradient of 5−20% EtOAc in petroleum ether) gave the title compound as an orange oil (250 mg, 87%). Recorded data are consistent with previous values:[45] ν_{max} (film) 3387, 2982, 2920, 1682, 1609, and 1520 cm^{-1}; ^1H NMR (400 MHz, 25.0 °C, $CDCl_3$) δ 7.92 (2 H, d, J = 8.3 Hz, Ar), 7.30 (2 H, d, J = 7.9 Hz, Ar), 6.98 (2 H, d, J = 7.9 Hz, Ar), 6.60 (2 H, d, J = 8.3 Hz, Ar), 5.08 (1 H, q, J = 6.9 Hz, CH), 2.43 (3 H, s, CH_3), 2.23 (3 H, s, CH_3) and 1.46 (3 H, d, J = 6.9 Hz, CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, 25.0 °C, $CDCl_3$) δ 200.5 (C═O), 144.5 (Ar), 144.3 (Ar), 132.2 (Ar), 129.8 (2 × ArH), 129.5 (2 × ArH), 128.6 (2 × ArH), 127.1 (Ar), 113.7 (2 × ArH), 53.6 (CH), 21.7 (CH_3), 20.4 (CH_3) and 19.7 (CH_3); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{17}H_{20}NO^+$ 254.1539; found 254.1542.

*1-(Naphth-2-yl)-2-(4-tolylamino)ethan-1-one (**16h**).* *p*-Toluidine (429 mg, 4.0 mmol, 1.0 equiv) and 2-bromo-1-(naphthalen-2-yl)ethan-1-one (996 mg, 4.0 mmol, 1.0 equiv) were treated with sodium hydrogen carbonate (336 mg, 4.0 mmol, 1.0 equiv) in ethanol (10 mL) and water (10 mL) according to General Procedure 2 for 2 h, and then the crude product was purified by recrystallization ($CHCl_3$/pentane) to give the title compound **16h** (980 mg, 89%) as a yellow solid: mp 130 °C dec; ν_{max} (film) 3395, 2970, 2924, 2862, 1682, 1620, 1528, 1057, and 1015 cm^{-1}; ^1H NMR (400 MHz, 22.0 °C, $CDCl_3$) δ 8.55 (1 H, s, naphthyl CH), 8.07 (1 H, dd, J = 8.6, 1.8 Hz, naphthyl CH), 8.01 (1 H, dd, J = 8.0, 1.3 Hz, naphthyl CH), 7.95 (1 H, d, J = 8.6 Hz, naphthyl CH), 7.91 (1 H, d, J = 8.4 Hz, naphthyl CH), 7.64 (1 H, ddd, J = 8.2, 6.9, 1.5 Hz, naphthyl CH), 7.59 (1 H, ddd, J = 8.2, 6.9, 1.5 Hz, naphthyl CH), 7.07 (2 H, d, J = 8.6 Hz, Ar), 6.72 (2 H, d, J = 8.4 Hz, Ar), 5.05 (1 H, br s, NH), 4.76 (2 H, s, CH_2) and 2.27 (3 H, s, CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, 22.7 °C, $CDCl_3$) δ 195.2 (C═O), 144.8 (naphthyl C), 135.9 (Ar), 132.5 (naphthyl C), 132.3 (naphthyl C), 129.9 (2 × ArH), 129.6 (naphthyl CH), 129.4 (naphthyl CH), 128.8 (naphthyl CH), 128.8 (naphthyl CH), 127.9 (naphthyl CH), 127.2 (Ar), 127.1 (naphthyl CH), 123.4 (naphthyl CH), 113.3 (2 × ArH), 50.9 (CH_2) and 20.4 (CH_3); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{19}H_{18}NO^+$ 276.1383; found 276.1391.

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*1-(4-Methoxyphenyl)-2-(4-tolylamino)ethan-1-one (**16i**).* *p*-Toluidine (429 mg, 4.0 mmol, 1.0 equiv) and 2-bromo-4′-methoxyacetophenone (916 mg, 4.0 mmol, 1.0 equiv) were treated with sodium hydrogen carbonate (336 mg, 4.0 mmol, 1.0 equiv) in ethanol (10 mL) and water (10 mL) according to General Procedure 2 for 2 h to give the title compound **16i** (888 mg, 87%) as a brown solid: mp 111−114 °C; ν_{max} (film) 3402, 3001, 2920, 2843, 1674, 1601, 1512, 1258, 1177, and 1034 cm^{-1}; ^1H NMR (400 MHz, 22.3 °C, $CDCl_3$) δ 8.00 (2 H, d, J = 8.9 Hz, Ar), 7.04 (2 H, d, J = 8.3 Hz, Ar), 6.98 (2 H, d, J = 8.9 Hz, Ar), 6.66 (2 H, d, J = 8.3 Hz, Ar), 5.00 (1 H, br s, NH), 4.56 (2 H, s, CH_2), 3.90 (3 H, s, OCH_3) and 2.26 (3 H, s, CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, 23.0 °C, $CDCl_3$) δ 193.6 (C═O), 164.0 (Ar), 144.9 (Ar), 130.1 (2 × ArH), 129.9 (2 × ArH), 128.0 (Ar), 127.1 (Ar), 114.0 (2 × ArH), 113.3 (2 × ArH), 55.5 (OCH_3), 50.4 (CH_2) and 20.4 (CH_3); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{16}H_{18}NO_2^+$ 256.1332; found 256.1333.

*1-(4-Nitrophenyl)-2-(4-tolylamino)ethan-1-one (**16j**).* *p*-Toluidine (429 mg, 4.0 mmol, 1.0 equiv) and 2-bromo-4′-nitroacetophenone (976 mg, 4.0 mmol, 1.0 equiv) were treated with sodium hydrogen carbonate (336 mg, 4.0 mmol, 1.0 equiv) in ethanol (10 mL) and water (10 mL) according to General Procedure 2 for 2 h, and then the crude product was purified by recrystallization ($CHCl_3$/pentane) to give the title compound **16j** (971 mg, 90%) as a red solid: mp 127 °C dec (lit. 147−150 °C);[46] ν_{max} (film) 3032, 2924, 2866, 1678, 1601, 1524, and 1346 cm^{-1}; ^1H NMR (400 MHz, 22.2 °C, $CDCl_3$) δ 8.37 (2 H, d, J = 8.8 Hz, Ar), 8.18 (2 H, d, J = 8.8 Hz, Ar), 7.05 (2 H, d, J = 8.4 Hz, Ar), 6.65 (2 H, d, J = 8.4 Hz, Ar), 4.74 (1 H, br s, NH), 4.66 (2 H, s, CH_2) and 2.26 (3 H, s, CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, 23.0 °C, $CDCl_3$) δ 194.1 (C═O), 150.7 (Ar), 144.4 (Ar), 139.4 (Ar), 130.0 (2 × ArH), 128.9 (2 × ArH), 127.6 (Ar), 124.1 (2 × ArH), 113.2 (2 × ArH), 51.4 (CH_2) and 20.4 (CH_3); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{15}H_{15}N_2O_3^+$ 271.1077; found 271.1084.

*1-(4-Cyanophenyl)-2-(4-tolylamino)ethan-1-one (**16k**).* *p*-Toluidine (429 mg, 4.0 mmol, 1.0 equiv) and 2-bromo-4′-cyanoacetophenone (896 mg, 4.0 mmol, 1.0 equiv) were treated with sodium hydrogen carbonate (336 mg, 4.0 mmol, 1.0 equiv) in ethanol (10 mL) and water (10 mL) according to General Procedure 2 for 2 h to give the title compound **16k** (921 mg, 92%) as an orange solid: mp 126 °C dec; ν_{max} (film) 3322, 2924, 2866, 2230, 1678, 1605, 1516, 1404, and 1277 cm^{-1}; ^1H NMR (400 MHz, 22.1 °C, $CDCl_3$) δ 8.11 (2 H, d, J = 8.5 Hz, Ar), 7.83 (2 H, d, J = 8.5 Hz, Ar), 7.04 (2 H, d, J = 8.4 Hz, Ar), 6.64 (2 H, d, J = 8.4 Hz, Ar), 4.62 (2 H, s, CH_2) and 2.26 (3 H, s, CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, 23.0 °C, $CDCl_3$) δ 194.3 (C═O), 144.4 (Ar), 137.9 (Ar), 132.7 (2 × ArH), 129.9 (2 × ArH), 128.2 (2 × ArH), 127.5 (Ar), 117.7 (Ar), 117.1 (C≡N), 113.2 (2 × ArH), 51.2 (CH_2) and 20.4 (CH_3); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{16}H_{15}N_2O^+$ 251.1179; found 251.1178.

*1-(4-Chlorophenyl)-2-(4-tolylamino)ethan-1-one (**16l**).* *p*-Toluidine (429 mg, 4.0 mmol, 1.0 equiv) and 2-bromo-4′-chloroacetophenone (934 mg, 4.0 mmol, 1.0 equiv) were treated with sodium hydrogen carbonate (336 mg, 4.0 mmol, 1.0 equiv) in ethanol (10 mL) and water (10 mL) according to General Procedure 2 for 2 h, and then the crude product was purified by recrystallization ($CHCl_3$/pentane) to give the title compound **16l** (866 mg, 83%) as a yellow solid: mp 127−130 °C (lit. 150−152 °C);[44] ν_{max} (film) 3391, 2916, 2859, 1682, 1589, and 1524 cm^{-1}; ^1H NMR (400 MHz, 22.4 °C, $CDCl_3$) δ 7.96 (2 H, d, J = 8.6 Hz, Ar), 7.49 (2 H, d, J = 8.6 Hz, Ar), 7.04 (2 H, d, J = 8.4 Hz, Ar), 6.64 (2 H, d, J = 8.4 Hz, Ar), 4.76 (1 H, br s, NH), 4.58 (2 H, s, CH_2) and 2.26 (3 H, s, CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, 22.8 °C, $CDCl_3$) δ 194.2 (C═O), 144.7 (Ar), 140.3 (Ar), 133.3 (Ar), 129.9 (2 × ArH), 129.2 (2 × ArH), 129.2 (2 × ArH), 127.2 (Ar), 113.2 (2 × ArH), 50.7 (CH_2) and 20.4 (CH_3); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{15}H_{15}ClNO^+$ 260.0837; found 260.0834.

*1-Cyclopropyl-2-(4-tolylamino)ethan-1-one (**16u**).* *p*-Toluidine (429 mg, 4.0 mmol, 1.0 equiv) and 2-bromo-1-cyclopropylethanone (652 mg, 4.0 mmol, 1.0 equiv) were treated with sodium hydrogen carbonate (336 mg, 4.0 mmol, 1.0 equiv) in ethanol (10 mL) and water (10 mL) according to General Procedure 2 for 16 h to give the title compound **16u** (562 mg, 74%) as a brown solid: mp 75−78 °C; ν_{max} (film) 3395, 3013, 2920, 2859, 1694, 1616, 1524, 1393, and 1069 cm^{-1}; ^1H NMR (400 MHz, 25.0 °C, $CDCl_3$) δ 7.01 (2 H, d, J = 8.5 Hz, Ar), 6.54 (2 H, d, J = 8.5 Hz, Ar), 4.52 (1 H, br s, NH), 4.15 (2 H, s, CH_2), 2.24 (3 H, s, CH_3), 2.01 (1 H, tt, J = 7.8, 4.6 Hz, cyclopropane CH), 1.16−1.12 (2 H, m, cyclopropane CH_2) and 1.01−0.95 (2 H, m, cyclopropane CH_2); $^{13}C\{^1H\}$ NMR (101 MHz, 25.0 °C, $CDCl_3$) δ 206.5 (C═O), 144.8 (Ar), 129.8 (2 × ArH), 126.9 (Ar), 113.0 (2 × ArH), 54.5 (CH_2), 20.4 (CH_3), 18.8 (cyclopropane CH) and 11.3 (2 × cyclopropane CH_2); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{12}H_{16}NO^+$ 190.1226; found 190.1230.

*1-(2-Tolyl)-2-(4-tolylamino)ethan-1-one (**16v**).* *p*-Toluidine (429 mg, 4.0 mmol, 1.0 equiv) and 2-bromo-2′-methylacetophenone (852 mg, 4.0 mmol, 1.0 equiv) were treated with sodium hydrogen carbonate (336 mg, 4.0 mmol, 1.0 equiv) in ethanol (10 mL) and water (10 mL) according to General Procedure 2 for 16 h, and then the crude product was purified by recrystallization ($CHCl_3$/pentane) to give the title compound **16v** (421 mg, 44%) as an orange solid: mp 124−127 °C; ν_{max} (film) 3387, 2924, 2851, 1690, 1620, and 1524 cm^{-1}; ^1H NMR (400 MHz, 25.0 °C, $CDCl_3$) δ 7.74−7.71 (1 H, m, Ar), 7.46−7.42 (1 H, m, Ar), 7.34−7.29 (2 H, m, Ar), 7.03 (2 H, d, J = 8.3 Hz, Ar), 6.62 (2 H, d, J = 8.3 Hz, Ar), 4.48 (2 H, s, CH_2), 2.55 (3 H, s, CH_3) and 2.25 (3 H, s, CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, 25.0 °C, $CDCl_3$) δ 198.8 (C═O), 144.9 (Ar), 138.9 (Ar), 135.4 (Ar), 132.3 (ArH), 132.1 (ArH), 129.9 (2 × ArH), 128.1 (ArH), 127.0 (Ar), 125.9 (ArH), 113.2 (2 × ArH), 52.6 (CH_2), 21.4 (CH_3) and 20.4 (CH_3); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{16}H_{18}NO^+$ 240.1383; found 240.1388.

General Procedure 3: Rh(II)-Catalyzed N−H Bond Insertion. Under argon, $Rh_2(OAc)_4$ (5 mol %) was added to a solution of α-aminoketone **16** (1.1 equiv) and triazole **4** (1.0 equiv) in toluene (0.03 M) in a flame-dried vial with freshly dried 4 Å molecular sieves. The vial was sealed with a Teflon cap and stirred at 80 °C (heating block) until complete (TLC, 2−4 h). The reaction mixture was concentrated in vacuo and purified by flash column chromatography (SiO_2, gradient from 10−30% EtOAc in petroleum ether) to give the 1,2-diamine product **17**.

*1-[(2-Oxo-2-(4-tolyl)ethyl)(4-tolyl)amino]-1-(4-tolyl)-2-(tosylamino)ethene (**17a**).* Triazole **4a** (94 mg, 0.30 mmol, 1.0 equiv) and α-aminoketone **16a** (79 mg, 0.33 mmol, 1.1 equiv) were treated with $Rh_2(OAc)_4$ (7 mg, 0.02 mmol, 5 mol %) in PhMe (10 mL) according to General Procedure 3 to give the title compound **17a** (139 mg, 88%) as a yellow solid: mp 61−69 °C; ν_{max} (film) 3250, 3032, 2924, 1690, 1609, 1512, and 1161 cm^{-1}; ^1H NMR (400 MHz, 22.4 °C, $CDCl_3$) δ 9.36 (1 H, d, J = 10.6 Hz, NH), 7.87 (2 H, d, J = 8.3 Hz, Ar), 7.65 (2 H, d, J = 8.3 Hz, Ar), 7.30 (2 H, d, J = 8.0 Hz, Ar), 7.17 (2 H, d, J = 8.3 Hz, Ar), 7.12 (2 H, d, J = 8.3 Hz, Ar), 7.10 (2 H, d, J = 8.3 Hz, Ar), 6.92 (1 H, d, J = 10.6 Hz, =CH), 6.75 (2 H, d, J = 8.6 Hz, Ar), 6.30 (2 H, d, J = 8.6 Hz, Ar), 4.66 (2 H, br s, CH_2), 2.45 (3 H, s, CH_3), 2.34 (3 H, s, CH_3), 2.33 (3 H, s, CH_3) and 2.20 (3 H, s, CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, 23.2 °C, $CDCl_3$) δ 197.2 (C═O), 145.3 (Ar), 143.3 (Ar), 143.0 (Ar), 137.9 (Ar), 137.4 (Ar), 132.7 (Ar), 131.8 (Ar), 129.7 (2 × ArH), 129.6 (2 × ArH), 129.5 (2 × ArH), 129.4 (2 × ArH), 128.3 (2 × ArH), 127.1 (Ar), 126.6 (2 × ArH), 125.9 (=C), 124.9 (2 × ArH), 121.8 (=CH), 112.2 (2 × ArH), 56.5 (CH_2), 21.8 (CH_3), 21.4 (CH_3), 21.1 (CH_3) and 20.3 (CH_3); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{32}H_{33}N_2O_3S^+$ 525.2206; found 525.2204.

*1-[(4-Chlorophenyl)(2-oxo-2-(4-tolyl)ethyl)amino]-1-(4-tolyl)-2-(tosylamino)ethene (**17b**).* Triazole **4a** (94 mg, 0.30 mmol, 1.0 equiv) and α-aminoketone **16b** (86 mg, 0.33 mmol, 1.1 equiv) were treated with $Rh_2(OAc)_4$ (7 mg, 0.02 mmol, 5 mol %) in PhMe (10 mL) according to General Procedure 3 to give the title compound **17b** (147 mg, 90%) as a yellow solid: mp 72 °C dec; ν_{max} (film) 3264, 3063, 2924, 1686, 1605, 1493, 1339, 1289, 1161, and 1092 cm^{-1}; ^1H NMR (400 MHz, 25.0 °C, $CDCl_3$) δ 9.40 (1 H, d, J = 10.6 Hz, NH), 7.89 (2 H, d, J = 8.2 Hz, COTol), 7.64 (2 H, d, J = 8.3 Hz, SO_2Tol), 7.32 (2 H, d, J = 7.9 Hz, Tol), 7.18−7.12 (6 H, m, Ar), 6.94 (1 H, d, J = 10.6 Hz, =CH), 6.84 (2 H, d, J = 9.1 Hz, NTol), 6.30 (2 H, d, J =

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9.1 Hz, NTol), 4.68 (2 H, br s, CH_2), 2.47 (3 H, s, CH_3), 2.40 (3 H, s, CH_3) and 2.36 (3 H, s, CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, 25.0 °C, $CDCl_3$) δ 196.8 (C═O), 145.7 (Ar), 144.5 (Ar), 143.4 (Ar), 138.1 (Ar), 137.8 (Ar), 132.2 (Ar), 131.6 (Ar), 129.7 (2 × ArH), 129.6 (2 × ArH), 129.5 (2 × ArH), 128.9 (2 × ArH), 128.4 (2 × ArH), 126.5 (2 × ArH), 125.5 (=C), 124.8 (2 × ArH), 123.0 (Ar), 122.1 (=CH), 113.5 (2 × ArH), 56.4 (OCH_3), 21.8 (CH_3), 21.5 (CH_3) and 21.1 (CH_3); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{31}H_{30}ClN_2O_3S^+$ 545.1660; found 545.1655.

*1-[(2-Oxo-2-(4-tolyl)ethyl)(3-trifluoromethylphenyl)amino]-1-(4-tolyl)-2-(tosylamino)ethene (**17c**).* Triazole **4a** (94 mg, 0.30 mmol, 1.0 equiv) and α-aminoketone **16c** (97 mg, 0.33 mmol, 1.1 equiv) were treated with $Rh_2(OAc)_4$ (7 mg, 0.02 mmol, 5 mol %) in PhMe (10 mL) according to General Procedure 3 to give the title compound **17c** (142 mg, 82%) as a white solid: mp 110 °C dec; ν_{max} (film) 3136, 3032, 2928, 1678, 1609, 1335, and 1165 cm^{-1}; ^1H NMR (400 MHz, 25.0 °C, $CDCl_3$) δ 9.40 (1 H, d, J = 10.6 Hz, NH), 7.86 (2 H, d, J = 8.3 Hz, Ar), 7.65 (2 H, d, J = 8.3 Hz, Ar), 7.31 (2 H, d, J = 7.9 Hz, Ar), 7.15−7.10 (6 H, m, Ar), 7.06 (1 H, dd, J = 8.1, 7.9 Hz, Ar), 6.97 (1 H, d, J = 10.6 Hz, =CH), 6.94 (1 H, d, J = 7.9 Hz, Ar), 6.64−6.60 (1 H, m, Ar), 6.57 (1 H, dd, J = 8.1, 2.6 Hz, Ar), 4.71 (2 H, br s, CH_2), 2.45 (3 H, s, CH_3), 2.34 (3 H, s, CH_3) and 2.32 (3 H, s, CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, 25.0 °C, $CDCl_3$) δ 196.6 (C═O), 146.2 (Ar), 145.8 (Ar), 143.4 (Ar), 137.8 (Ar), 137.7 (Ar), 131.8 (Ar), 131.8 (q, J = 33.3 Hz, Ar), 131.5 (Ar), 129.8 (ArH), 129.8 (2 × ArH), 129.7 (2 × ArH), 129.6 (2 × ArH), 128.4 (2 × ArH), 126.6 (2 × ArH), 124.7 (2 × ArH), 124.5 (=C), 122.5 (=CH), 115.5 (ArH), 114.9 (q, J = 4.1 Hz, ArH), 108.5 (q, J = 2.4 Hz, ArH), 56.5 (CH_2), 21.9 (CH_3), 21.4 (CH_3) and 21.1 (CH_3); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{32}H_{30}F_3N_2O_3S^+$ 579.1924; found 579.1928.

*1-[(4-Methoxyphenyl)(2-oxo-2-(4-tolyl)ethyl)amino]-1-(4-tolyl)-2-(tosylamino)ethene (**17d**).* Triazole **4a** (94 mg, 0.30 mmol, 1.0 equiv) and α-aminoketone **16d** (84 mg, 0.33 mmol, 1.1 equiv) were treated with $Rh_2(OAc)_4$ (7 mg, 0.02 mmol, 5 mol %) in PhMe (10 mL) according to General Procedure 3 to give the title compound **17d** (144 mg, 89%) as a yellow solid: mp 45−50 °C; ν_{max} (film) 3252, 2924, 2855, 1690, 1609, 1512, 1250, 1161, and 1034 cm^{-1}; ^1H NMR (500 MHz, 25.1 °C, $CDCl_3$) δ 9.32 (1 H, d, J = 10.6 Hz, NH), 7.86 (2 H, d, J = 8.3 Hz, COTol), 7.63 (2 H, d, J = 8.3 Hz, SO_2Tol), 7.28 (2 H, d, J = 8.0 Hz, COTol), 7.16 (2 H, d, J = 8.3 Hz, Tol), 7.11 (2 H, d, J = 8.3 Hz, SO_2Tol), 7.10 (2 H, d, J = 8.0 Hz, Tol), 6.88 (1 H, d, J = 10.6 Hz, =CH), 6.53 (2 H, d, J = 9.1 Hz, NC_6H_4OMe), 6.32 (2 H, d, J = 9.1 Hz, NC_6H_4OMe), 4.63 (2 H, br s, CH_2), 3.70 (3 H, s, OCH_3), 2.44 (3 H, s, COTol), 2.33 (3 H, s, CH_3) and 2.33 (3 H, s, CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, 25.0 °C, $CDCl_3$) δ 197.4 (C═O), 152.4 (Ar), 145.4 (Ar), 143.1 (Ar), 139.9 (Ar), 138.0 (Ar), 137.5 (Ar), 132.8 (Ar), 131.9 (Ar), 129.6 (2 × ArH), 129.6 (2 × ArH), 129.5 (2 × ArH), 128.3 (2 × ArH), 126.7 (2 × ArH), 126.2 (=C), 124.9 (2 × ArH), 121.8 (=CH), 114.7 (2 × ArH), 113.3 (2 × ArH), 56.8 (CH_2), 55.6 (OCH_3), 21.8 (CH_3), 21.5 (CH_3) and 21.1 (CH_3); HRMS (ESI-TOF) m/z $[M - H]^-$ calcd for $C_{32}H_{31}N_2O_4S^-$ 539.2010; found 539.2017.

*1-[(1-Oxo-1-(4-tolyl)prop-2-yl)(4-tolyl)amino]-1-(4-tolyl)-2-(tosylamino)ethene (**17g**).* Triazole **4a** (94 mg, 0.30 mmol, 1.0 equiv) and α-aminoketone **16g** (84 mg, 0.33 mmol, 1.1 equiv) were treated with $Rh_2(OAc)_4$ (7 mg, 0.02 mmol, 5 mol %) in PhMe (10 mL) according to General Procedure 3 to give the title compound **17g** (142 mg, 88%) as a yellow solid: mp 65 °C dec; ν_{max} (film) 3094, 3028, 2924, 1674, 1605, 1512, 1343, 1289, 1235, and 1157 cm^{-1}; ^1H NMR (500 MHz, 25.0 °C, $CDCl_3$) δ 10.51 (1 H, d, J = 10.8 Hz, NH), 8.09 (2 H, d, J = 8.2 Hz, COTol), 7.72 (2 H, d, J = 8.3 Hz, SO_2Tol), 7.37 (2 H, d, J = 8.2 Hz, COTol), 7.31 (1 H, d, J = 10.8 Hz, =CH), 7.15 (2 H, d, J = 8.3 Hz, SO_2Tol), 7.11 (2 H, d, J = 8.1 Hz, Tol), 7.04 (2 H, d, J = 8.1 Hz, Tol), 6.70 (2 H, d, J = 8.7 Hz, NTol), 6.25 (2 H, d, J = 8.7 Hz, NTol), 5.48 (1 H, q, J = 7.4 Hz, CH), 2.49 (3 H, s, COTol), 2.35 (3 H, s, SO_2Tol), 2.28 (3 H, s, Tol), 2.13 (3 H, s, NTol) and 1.11 (3 H, d, J = 7.4 Hz, CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, 25.0 °C, $CDCl_3$) δ 203.3 (C═O), 145.5 (Ar), 143.2 (Ar), 143.0 (Ar), 138.1 (Ar), 136.6 (Ar), 134.6 (Ar), 131.4 (Ar), 129.9 (2 × ArH), 129.7 (2 × ArH), 129.5 (2 × ArH), 129.5 (2 × ArH), 128.7 (2 × ArH), 126.9 (Ar), 126.7 (2 × ArH), 125.5 (=CH), 123.9 (2 × ArH), 121.2 (=C), 112.3 (2 × ArH), 57.7 (CH), 21.8 (CH_3), 21.5 (CH_3), 21.0 (CH_3), 20.2 (CH_3) and 16.0 (CH_3); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{33}H_{35}N_2O_3S^+$ 539.2363; found 539.2368.

*1-[(2-(Naphth-2-yl)-2-oxoethyl)(4-tolyl)amino]-1-(4-tolyl)-2-(tosylamino)ethene (**17h**).* Triazole **4a** (94 mg, 0.30 mmol, 1.0 equiv) and α-aminoketone **16h** (91 mg, 0.33 mmol, 1.1 equiv) were treated with $Rh_2(OAc)_4$ (7 mg, 0.02 mmol, 5 mol %) in PhMe (10 mL) according to General Procedure 3 to give the title compound **17h** (159 mg, 95%) as a yellow solid: mp 58 °C dec; ν_{max} (film) 3240, 3032, 2920, 2862, 1678, 1512, 1161, and 1092 cm^{-1}; ^1H NMR (400 MHz, 25.4 °C, $CDCl_3$) δ 9.31 (1 H, d, J = 10.7 Hz, NH), 8.46 (1 H, s, naphthyl CH), 8.02 (1 H, dd, J = 8.6, 1.7 Hz, naphthyl CH), 7.95 (1 H, d, J = 7.5 Hz, naphthyl CH), 7.94 (1 H, d, J = 8.7 Hz, naphthyl CH), 7.91 (1 H, d, J = 8.0 Hz, naphthyl CH), 7.66 (2 H, d, J = 8.3 Hz, Ar), 7.65−7.63 (1 H, m, naphthyl CH), 7.59 (1 H, ddd, J = 8.1, 6.9, 1.3 Hz, naphthyl CH), 7.21 (2 H, d, J = 8.3 Hz, Ar), 7.13 (2 H, d, J = 8.1 Hz, Ar), 7.08 (2 H, d, J = 8.1 Hz, Ar), 6.94 (1 H, d, J = 10.7 Hz, =CH), 6.77 (2 H, d, J = 7.9 Hz, Ar), 6.34 (2 H, d, J = 8.7 Hz, Ar), 4.81 (2 H, br s, CH_2), 2.34 (3 H, s, CH_3), 2.26 (3 H, s, CH_3) and 2.20 (3 H, s, CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, 24.8 °C, $CDCl_3$) δ 197.6 (C═O), 143.3 (Ar), 143.1 (naphthyl C), 138.0 (Ar), 137.5 (naphthyl C), 136.1 (naphthyl C), 132.8 (Ar), 132.3 (Ar), 131.7 (Ar), 130.0 (naphthyl CH), 129.7 (2 × ArH), 129.6 (2 × ArH), 129.6 (naphthyl CH), 129.4 (2 × ArH), 129.1 (naphthyl CH), 128.8 (naphthyl CH), 127.9 (naphthyl CH), 127.3 (Ar), 127.2 (naphthyl CH), 126.7 (2 × ArH), 125.9 (=C), 125.0 (2 × ArH), 123.6 (naphthyl CH), 122.0 (=CH), 112.3 (2 × ArH), 56.8 (CH_2), 21.4 (CH_3), 21.1 (CH_3) and 20.3 (CH_3); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{35}H_{33}N_2O_3S^+$ 561.2206; found 561.2208.

*1-[(2-(4-Methoxyphenyl)-2-oxoethyl)(4-tolyl)amino]-1-(4-tolyl)-2-(tosylamino)ethene (**17i**).* Triazole **4a** (94 mg, 0.30 mmol, 1.0 equiv) and α-aminoketone **16i** (84 mg, 0.33 mmol, 1.1 equiv) were treated with $Rh_2(OAc)_4$ (7 mg, 0.02 mmol, 5 mol %) in PhMe (10 mL) according to General Procedure 3 to give the title compound **17i** (123 mg, 76%) as a brown solid: mp 69−74 °C; ν_{max} (film) 3225, 3028, 2920, 2859, 1674, 1597, 1512, 1339, 1265, 1234, 1161, and 1092 cm^{-1}; ^1H NMR (400 MHz, 25.4 °C, $CDCl_3$) δ 9.45 (1 H, d, J = 10.6 Hz, NH), 7.95 (2 H, d, J = 8.9 Hz, Ar), 7.63 (2 H, d, J = 8.3 Hz, Ar), 7.16 (2 H, d, J = 8.3 Hz, Ar), 7.12 (2 H, d, J = 8.0 Hz, Ar), 7.10 (2 H, d, J = 8.6 Hz, Ar), 6.95 (2 H, d, J = 8.9 Hz, Ar), 6.90 (1 H, d, J = 10.6 Hz, =CH), 6.74 (2 H, d, J = 8.0 Hz, Ar), 6.29 (2 H, d, J = 8.6 Hz, Ar), 4.62 (2 H, br s, CH_2), 3.89 (3 H, s, OCH_3), 2.34 (3 H, s, CH_3), 2.32 (3 H, s, CH_3) and 2.19 (3 H, s, CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, 25.1 °C, $CDCl_3$) δ 196.0 (C═O), 164.4 (Ar), 143.4 (Ar), 143.0 (Ar), 138.1 (Ar), 137.4 (Ar), 132.8 (Ar), 130.6 (2 × ArH), 129.7 (2 × ArH), 129.6 (2 × ArH), 129.4 (2 × ArH), 127.4 (Ar), 127.1 (Ar), 126.7 (2 × ArH), 125.9 (=C), 124.9 (2 × ArH), 121.9 (=CH), 114.0 (2 × ArH), 112.2 (2 × ArH), 56.3 (CH_2), 55.6 (OCH_3), 21.5 (CH_3), 21.1 (CH_3) and 20.3 (CH_3); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{32}H_{33}N_2O_4S^+$ 541.2156; found 541.2158.

*1-[(2-(4-Nitrophenyl)-2-oxoethyl)(4-tolyl)amino]-1-(4-tolyl)-2-(tosylamino)ethene (**17j**).* Triazole **4a** (94 mg, 0.30 mmol, 1.0 equiv) and α-aminoketone **16j** (89 mg, 0.33 mmol, 1.1 equiv) were treated with $Rh_2(OAc)_4$ (7 mg, 0.02 mmol, 5 mol %) in PhMe (10 mL) according to General Procedure 3 to give the title compound **17j** (70 mg, 42%) as a pink solid. Under the reaction conditions, there was also some cyclodehydration to the corresponding pyrrole **18j** (80 mg, 50%): mp 115 °C dec; ν_{max} (film) 3183, 2924, 2856, 1694, 1516, 1343, 1215, 1161, and 1092 cm^{-1}; ^1H NMR (400 MHz, 24.9 °C, $CDCl_3$) δ 8.78 (1 H, d, J = 10.8 Hz, NH), 8.34 (2 H, d, J = 8.8 Hz, Ar), 8.11 (2 H, d, J = 8.8 Hz, Ar), 7.64 (2 H, d, J = 8.4 Hz, Ar), 7.17 (2 H, d, J = 8.4 Hz, Ar), 7.15 (2 H, d, J = 8.0 Hz, Ar), 7.11 (2 H, d, J = 8.6 Hz, Ar), 6.88 (1 H, d, J = 10.8 Hz, =CH), 6.76 (2 H, d, J = 8.0 Hz, Ar), 6.28 (2 H, d, J = 8.6 Hz, Ar), 4.71 (2 H, s, CH_2), 2.37 (3 H, s, CH_3), 2.33 (3 H, s, CH_3) and 2.21 (3 H, s, CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, 25.0 °C, $CDCl_3$) δ 196.5 (C═O), 150.9 (Ar), 143.3 (Ar), 143.0 (Ar), 138.7 (Ar), 137.9 (Ar), 137.8 (Ar), 132.4 (Ar), 129.8 (2 × ArH), 129.7 (2 × ArH), 129.5 (2 × ArH), 129.3 (2 × ArH), 127.8

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(Ar), 126.7 (2 × ArH), 125.4 (=C), 125.0 (2 × ArH), 124.1 (2 × ArH), 121.6 (=CH), 112.3 (2 × ArH), 57.0 (CH_2), 21.5 (CH_3), 21.1 (CH_3) and 20.3 (CH_3); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{31}H_{30}N_3O_5S^+$ 556.1901; found 556.1883.

*1-[(2-(4-Cyanophenyl)-2-oxoethyl)(4-tolyl)amino]-1-(4-tolyl)-2-(tosylamino)ethene (**17k**).* Triazole **4a** (94 mg, 0.30 mmol, 1.0 equiv) and α-aminoketone **16k** (83 mg, 0.33 mmol, 1.1 equiv) were treated with $Rh_2(OAc)_4$ (7 mg, 0.02 mmol, 5 mol %) in PhMe (10 mL) according to General Procedure 3 to give the title compound **17k** (65 mg, 40%) as a yellow solid. Under the reaction conditions, there was also some cyclodehydration to the corresponding pyrrole **18k** (78 mg, 50%): mp 113 °C dec; ν_{max} (film) 3245, 3028, 2924, 2856, 2230, 1690, 1512, 1161, and 1092 cm^{-1}; ^1H NMR (500 MHz, 25.0 °C, $CDCl_3$) δ 8.81 (1 H, d, J = 10.8 Hz, NH), 8.04 (2 H, d, J = 8.8 Hz, Ar), 7.80 (2 H, d, J = 8.8 Hz, Ar), 7.64 (2 H, d, J = 8.3 Hz, Ar), 7.16 (2 H, d, J = 7.9 Hz, Ar), 7.14 (2 H, d, J = 8.7 Hz, Ar), 7.11 (2 H, d, J = 8.3 Hz, Ar), 6.88 (1 H, d, J = 10.8 Hz, =CH), 6.75 (2 H, d, J = 7.9 Hz, Ar), 6.27 (2 H, d, J = 8.7 Hz, Ar), 4.68 (2 H, s, CH_2), 2.37 (3 H, s, CH_3), 2.33 (3 H, s, CH_3) and 2.20 (3 H, s, CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, 26.0 °C, $CDCl_3$) δ 196.7 (C═O), 143.2 (Ar), 143.0 (Ar), 137.9 (Ar), 137.7 (Ar), 137.2 (Ar), 132.7 (2 × ArH), 132.4 (Ar), 129.8 (2 × ArH), 129.7 (2 × ArH), 129.5 (2 × ArH), 128.6 (2 × ArH), 127.8 (Ar), 126.7 (2 × ArH), 125.4 (=C), 125.0 (2 × ArH), 121.6 (=CH), 117.6 (Ar), 117.5 (C≡N), 112.3 (2 × ArH), 56.9 (CH_2), 21.5 (CH_3), 21.1 (CH_3) and 20.3 (CH_3); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{32}H_{30}N_3O_3S^+$ 536.2002; found 536.2005.

*1-[(2-(4-Chlorophenyl)-2-oxoethyl)(4-tolyl)amino]-1-(4-tolyl)-2-(tosylamino)ethene (**17l**).* Triazole **4a** (94 mg, 0.30 mmol, 1.0 equiv) and α-aminoketone **16l** (86 mg, 0.33 mmol, 1.1 equiv) were treated with $Rh_2(OAc)_4$ (7 mg, 0.02 mmol, 5 mol %) in PhMe (10 mL) according to General Procedure 3 to give the title compound **17l** (109 mg, 67%) as a yellow solid. Under the reaction conditions, there was also some cyclodehydration to the corresponding pyrrole **18l** (50 mg, 32%): mp 63 °C dec; ν_{max} (film) 3175, 3028, 2920, 1686, 1589, 1512, 1339, 1223, 1161, and 1092 cm^{-1}; ^1H NMR (400 MHz, 26.0 °C, $CDCl_3$) δ 9.09 (1 H, d, J = 10.7 Hz, NH), 7.89 (2 H, d, J = 8.6 Hz, Ar), 7.63 (2 H, d, J = 8.3 Hz, Ar), 7.47 (2 H, d, J = 8.6 Hz, Ar), 7.15 (2 H, d, J = 8.3 Hz, Ar), 7.12 (2 H, d, J = 8.6 Hz, Ar), 7.10 (2 H, d, J = 8.6 Hz, Ar), 6.90 (1 H, d, J = 10.7 Hz, =CH), 6.75 (2 H, d, J = 8.7 Hz, Ar), 6.28 (2 H, d, J = 8.7 Hz, Ar), 4.64 (2 H, br s, CH_2), 2.35 (3 H, s, CH_3), 2.33 (3 H, s, CH_3) and 2.20 (3 H, s, CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, 26.0 °C, $CDCl_3$) δ 196.6 (C═O), 143.2 (Ar), 143.1 (Ar), 140.9 (Ar), 137.9 (Ar), 137.6 (Ar), 132.6 (Ar), 132.6 (Ar), 129.7 (2 × ArH), 129.6 (2 × ArH), 129.6 (2 × ArH), 129.4 (2 × ArH), 129.2 (2 × ArH), 127.5 (Ar), 126.7 (2 × ArH), 125.7 (=C), 124.9 (2 × ArH), 121.8 (=C), 112.2 (2 × ArH), 56.6 (CH_2), 21.5 (CH_3), 21.1 (CH_3) and 20.3 (CH_3); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{31}H_{30}ClN_2O_3S^+$ 545.1660; found 545.1659.

*1-[(2-Oxo-2-(4-tolyl)ethyl)(4-tolyl)amino]-1-(thiophen-2-yl)-2-(tosylamino)ethene (**17m**).* Triazole **4m** (92 mg, 0.30 mmol, 1.0 equiv) and α-aminoketone **16a** (79 mg, 0.33 mmol, 1.1 equiv) were treated with $Rh_2(OAc)_4$ (7 mg, 0.02 mmol, 5 mol %) in PhMe (10 mL) according to General Procedure 3 to give the title compound **17m** (124 mg, 80%) as an orange solid: mp 126 °C dec; ν_{max} (film) 3148, 3032, 2920, 1678, 1609, 1516, 1339, 1231, 1161, and 1092 cm^{-1}; ^1H NMR (400 MHz, 25.0 °C, $CDCl_3$) δ 9.39 (1 H, d, J = 10.7 Hz, NH), 7.88 (2 H, d, J = 8.3 Hz, Ar), 7.64 (2 H, d, J = 8.3 Hz, Ar), 7.31 (2 H, d, J = 8.3 Hz, Ar), 7.12 (1 H, dd, J = 5.1, 1.2 Hz, thiophene CH), 7.10 (2 H, d, J = 8.3 Hz, Ar), 6.92 (1 H, dd, J = 5.1, 3.6 Hz, thiophene CH), 6.90 (1 H, d, J = 10.7 Hz, =CH), 6.84 (1 H, dd, J = 3.6, 1.2 Hz, thiophene CH), 6.77 (2 H, d, J = 8.3 Hz, Ar), 6.31 (2 H, d, J = 8.3 Hz, Ar), 4.71 (2 H, br s, CH_2), 2.45 (3 H, s, CH_3), 2.33 (3 H, s, CH_3) and 2.19 (3 H, s, CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, 25.0 °C, $CDCl_3$) δ 197.2 (C═O), 145.5 (Ar), 143.1 (Ar), 142.6 (thiophene C2), 141.0 (Ar), 137.8 (Ar), 131.8 (Ar), 129.7 (2 × ArH), 129.6 (2 × ArH), 129.4 (2 × ArH), 128.3 (2 × ArH), 127.7 (thiophene CH), 127.5 (Ar), 126.7 (2 × ArH), 123.8 (thiophene CH), 122.9 (thiophene CH), 122.0 (=CH), 121.7 (=C), 112.4 (2 × ArH), 56.5 (CH_2), 21.8 (CH_3), 21.5 (CH_3) and 20.3 (CH_3); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{29}H_{29}N_2O_3S_2^+$ 517.1614; found 517.1617.

*1-(4-Methoxyphenyl)-1-[(2-oxo-2-(4-tolyl)ethyl)(4-tolyl)amino]-2-(tosylamino)ethene (**17n**).* Triazole **4n** (99 mg, 0.30 mmol, 1.0 equiv) and α-aminoketone **16a** (79 mg, 0.33 mmol, 1.1 equiv) were treated with $Rh_2(OAc)_4$ (7 mg, 0.02 mmol, 5 mol %) in PhMe (10 mL) according to General Procedure 3 to give the title compound **17n** (152 mg, 94%) as an orange solid: mp 66−70 °C; ν_{max} (film) 3275, 3032, 2924, 1682, 1601, 1512, 1339, 1250, and 1161 cm^{-1}; ^1H NMR (400 MHz, 25.0 °C, $CDCl_3$) δ 9.27 (1 H, d, J = 10.6 Hz, NH), 7.86 (2 H, d, J = 8.3 Hz, Ar), 7.64 (2 H, d, J = 8.3 Hz, Ar), 7.28 (2 H, d, J = 8.3 Hz, Ar), 7.19 (2 H, d, J = 8.8 Hz, Ar), 7.11 (2 H, d, J = 8.3 Hz, Ar), 6.82 (2 H, d, J = 8.8 Hz, Ar), 6.81 (1 H, d, J = 10.6 Hz, =CH), 6.74 (2 H, d, J = 8.6 Hz, Ar), 6.29 (2 H, d, J = 8.6 Hz, Ar), 4.63 (2 H, br s, CH_2), 3.79 (3 H, s, CH_3), 2.44 (3 H, s, CH_3), 2.34 (3 H, s, CH_3) and 2.19 (3 H, s, CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, 25.0 °C, $CDCl_3$) δ 197.2 (C═O), 159.3 (Ar), 145.3 (Ar), 143.3 (Ar), 143.0 (Ar), 138.0 (Ar), 131.9 (Ar), 129.7 (2 × ArH), 129.5 (2 × ArH), 129.4 (2 × ArH), 128.3 (2 × ArH), 128.1 (Ar), 127.2 (Ar), 126.7 (2 × ArH), 126.3 (2 × ArH), 125.8 (=C), 120.8 (=CH), 114.3 (2 × ArH), 112.3 (2 × ArH), 56.4 (CH_2), 55.4 (OCH_3), 21.8 (CH_3), 21.5 (CH_3) and 20.3 (CH_3); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{32}H_{33}N_2O_4S^+$ 541.2156; found 541.2148.

*1-(Cyclohexen-1-yl)-1-[(2-oxo-2-(4-tolyl)ethyl)(4-tolyl)amino]-2-(tosylamino)ethene (**17o**).* Triazole **4o** (91 mg, 0.30 mmol, 1.0 equiv) and α-aminoketone **16a** (79 mg, 0.33 mmol, 1.1 equiv) were treated with $Rh_2(OAc)_4$ (7 mg, 0.02 mmol, 5 mol %) in PhMe (10 mL) according to General Procedure 3 to give the title compound **17o** (126 mg, 82%) as a yellow solid: mp 140 °C dec; ν_{max} (film) 3152, 3032, 2924, 1678, 1609, 1516, 1343, and 1161 cm^{-1}; ^1H NMR (400 MHz, 25.0 °C, $CDCl_3$) δ 9.41 (1 H, d, J = 10.7 Hz, NH), 7.90 (2 H, d, J = 8.2 Hz, Ar), 7.64 (2 H, d, J = 8.3 Hz, Ar), 7.32 (2 H, d, J = 8.2 Hz, Ar), 7.09 (2 H, d, J = 8.3 Hz, Ar), 6.79 (2 H, d, J = 8.6 Hz, Ar), 6.51 (1 H, d, J = 10.7 Hz, =CH), 6.18 (2 H, d, J = 8.6 Hz, Ar), 5.46 (1 H, t, J = 4.2 Hz, =CH), 4.62 (2 H, br s, CH_2), 2.46 (3 H, s, CH_3), 2.31 (3 H, s, CH_3), 2.19 (3 H, s, CH_3), 2.15−2.08 (2 H, m, CH_2), 2.07−2.00 (2 H, m, CH_2), 1.72−1.64 (2 H, m, CH_2) and 1.62−1.52 (2 H, m, CH_2); $^{13}C\{^1H\}$ NMR (101 MHz, 25.0 °C, $CDCl_3$) δ 197.6 (C═O), 145.3 (Ar), 143.3 (Ar), 142.9 (Ar), 137.8 (Ar), 132.0 (Ar), 129.9 (=C), 129.6 (2 × ArH), 129.5 (2 × ArH), 129.3 (2 × ArH), 128.4 (=C), 128.3 (2 × ArH), 126.6 (2 × ArH), 126.5 (Ar), 123.5 (=CH), 121.3 (=CH), 111.7 (2 × ArH), 57.2 (CH_2), 25.5 (CH_2), 24.9 (CH_2), 22.5 (CH_2), 22.2 (CH_2), 21.8 (CH_3), 21.4 (CH_3) and 20.3 (CH_3); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{31}H_{35}N_2O_3S^+$ 515.2363; found 515.2355.

*2-(4-Methoxybenzenesulfonylamino)-1-[(2-oxo-2-(4-tolyl)ethyl)-(4-tolyl)amino]-1-(4-tolyl)ethene (**17p**).* Triazole **4r** (99 mg, 0.30 mmol, 1.0 equiv) and α-aminoketone **16a** (79 mg, 0.33 mmol, 1.1 equiv) were treated with $Rh_2(OAc)_4$ (7 mg, 0.02 mmol, 5 mol %) in PhMe (10 mL) according to General Procedure 3 to give the title compound **17p** (142 mg, 87%) as a yellow solid: mp 60−66 °C; ν_{max} (film) 3148, 3028, 2920, 1678, 1597, 1516, 1339, 1304, 1258, 1157, and 1092 cm^{-1}; ^1H NMR (400 MHz, 25.0 °C, $CDCl_3$) δ 9.31 (1 H, d, J = 10.7 Hz, NH), 7.86 (2 H, d, J = 8.3 Hz, Ar), 7.69 (2 H, d, J = 9.0 Hz, Ar), 7.28 (2 H, d, J = 7.8 Hz, Ar), 7.16 (2 H, d, J = 8.3 Hz, Ar), 7.10 (2 H, d, J = 7.8 Hz, Ar), 6.90 (1 H, d, J = 10.7 Hz, =CH), 6.77 (2 H, d, J = 9.0 Hz, Ar), 6.76 (2 H, d, J = 8.4 Hz, Ar), 6.30 (2 H, d, J = 8.4 Hz, Ar), 4.65 (2 H, br s, CH_2), 3.79 (3 H, s, OCH_3), 2.44 (3 H, s, CH_3), 2.32 (3 H, s, CH_3) and 2.19 (3 H, s, CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, 25.0 °C, $CDCl_3$) δ 197.2 (C═O), 162.6 (Ar), 145.3 (Ar), 143.4 (Ar), 137.4 (Ar), 132.8 (Ar), 132.7 (Ar), 131.9 (Ar), 129.7 (2 × ArH), 129.6 (2 × ArH), 129.5 (2 × ArH), 128.8 (2 × ArH), 128.3 (2 × ArH), 127.2 (Ar), 125.8 (=C), 124.9 (2 × ArH), 122.0 (=CH), 113.9 (2 × ArH), 112.2 (2 × ArH), 56.5 (OCH_3), 55.4 (CH_3), 21.8 (CH_3), 21.1 (CH_3) and 20.3 (CH_3); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{32}H_{33}N_2O_4S^+$ 541.2156; found 541.2158.

*2-(4-Nitrobenzenesulfonylamino)-1-[(2-oxo-2-(4-tolyl)ethyl)(4-tolyl)amino]-1-(4-tolyl)ethene (**17q**).* Triazole **4q** (103 mg, 0.30 mmol, 1.0 equiv) and α-aminoketone **16a** (79 mg, 0.33 mmol, 1.1 equiv) were treated with $Rh_2(OAc)_4$ (7 mg, 0.02 mmol, 5 mol %) in

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PhMe (10 mL) according to General Procedure 3 to give the title compound **17q** (66 mg, 40%) as a yellow solid: mp 143 °C dec; ν_{max} (film) 3102, 3032, 2920, 1678, 1605, 1516, 1346, 1231, and 1165 cm^{-1}; ^1H NMR (400 MHz, 25.0 °C, $CDCl_3$) δ 9.77 (1 H, d, J = 10.2 Hz, NH), 8.12 (2 H, d, J = 9.0 Hz, Ar), 7.88 (2 H, d, J = 9.0 Hz, Ar), 7.85 (2 H, d, J = 8.3 Hz, Ar), 7.29 (2 H, d, J = 8.6 Hz, Ar), 7.18 (2 H, d, J = 8.3 Hz, Ar), 7.12 (2 H, d, J = 7.9 Hz, Ar), 6.88 (1 H, d, J = 10.2 Hz, =CH), 6.68 (2 H, d, J = 7.9 Hz, Ar), 6.26 (2 H, d, J = 8.6 Hz, Ar), 4.65 (2 H, br s, CH_2), 2.44 (3 H, s, CH_3), 2.34 (3 H, s, CH_3) and 2.16 (3 H, s, CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, 25.0 °C, $CDCl_3$) δ 197.9 (C═O), 149.7 (Ar), 146.6 (Ar), 145.9 (Ar), 143.7 (Ar), 138.2 (Ar), 132.1 (Ar), 131.5 (Ar), 129.7 (2 × ArH), 129.7 (2 × ArH), 129.6 (2 × ArH), 128.3 (2 × ArH), 128.0 (Ar), 127.9 (=C), 127.7 (2 × ArH), 125.2 (2 × ArH), 124.0 (2 × ArH), 120.6 (=CH), 112.5 (2 × ArH), 56.6 (CH_2), 21.8 (CH_3), 21.1 (CH_3) and 20.1 (CH_3); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{31}H_{30}N_3O_5S^+$ 556.1901; found 556.1903.

*2-(Mesylamino)-1-[(2-oxo-2-(4-tolyl)ethyl)(4-tolyl)amino]-1-(4-tolyl)ethene (**17r**).* Triazole **4p** (71 mg, 0.30 mmol, 1.0 equiv) and α-aminoketone **16a** (79 mg, 0.33 mmol, 1.1 equiv) were treated with $Rh_2(OAc)_4$ (7 mg, 0.02 mmol, 5 mol %) in PhMe (10 mL) according to General Procedure 3 to give the title compound **17r** (65 mg, 48%) as a yellow solid: mp 111−116 °C; ν_{max} (film) 2924, 1682, 1609, 1516, 1331, 1231, and 1150 cm^{-1}; ^1H NMR (400 MHz, 25.0 °C, $CDCl_3$) δ 9.18 (1 H, d, J = 10.4 Hz, NH), 7.91 (2 H, d, J = 8.2 Hz, Ar), 7.29 (2 H, d, J = 7.9 Hz, Ar), 7.24 (2 H, d, J = 8.2 Hz, Ar), 7.14 (2 H, d, J = 7.9 Hz, Ar), 6.98 (2 H, d, J = 8.5 Hz, Ar), 6.85 (1 H, d, J = 10.4 Hz, =CH), 6.54 (2 H, d, J = 8.5 Hz, Ar), 4.76 (2 H, br s, CH_2), 2.90 (3 H, s, CH_3), 2.43 (3 H, s, CH_3), 2.35 (3 H, s, CH_3) and 2.23 (3 H, s, CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, 25.0 °C, $CDCl_3$) δ 197.5 (C═O), 145.5 (Ar), 143.7 (Ar), 137.7 (Ar), 132.6 (Ar), 131.8 (Ar), 130.0 (2 × ArH), 129.7 (2 × ArH), 129.6 (2 × ArH), 128.3 (2 × ArH), 127.8 (Ar), 125.7 (=C), 125.0 (2 × ArH), 121.4 (=CH), 112.6 (2 × ArH), 56.4 (CH_2), 42.0 (CH_3), 21.8 (CH_3), 21.1 (CH_3) and 20.3 (CH_3); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{26}H_{29}N_2O_3S^+$ 449.1893; found 449.1901.

General Procedure 4: Cyclodehydration. Under argon, boron trifluoride diethyl etherate (3.0 equiv) was added in one portion to a solution of 1,2-diamine **17** (1.0 equiv) in CH_2Cl_2 (0.03 M) in a flame-dried vial. The vial was sealed with a Teflon cap and heated at 80 °C (heating block) for 15 min. The reaction mixture was cooled to ambient temperature; saturated aqueous $NaHCO_3$ was added, and the aqueous phase was extracted with CH_2Cl_2 (3 × 30 mL $mmol^{-1}$). The combined organic layers were washed with brine, dried ($MgSO_4$), and concentrated in vacuo. Purification by column chromatography (SiO_2, gradient of 10−30% EtOAc in petroleum ether) gave the pyrrole **18**.

General Procedure 5: One-Pot Pyrrole Synthesis. Under argon, copper(I) thiophene-2-carboxylate (5 mol %) was added to a solution of alkyne **21** (1.1 equiv) in CH_2Cl_2 (0.03 M) in a flame-dried vial with freshly dried 4 Å molecular sieves. The mixture was cooled to 0 °C (ice bath) and stirred for 10 min. Then sulfonyl azide **22** (1.1 equiv) was added, and the reaction mixture was allowed to reach ambient temperature. When the CuAAC reaction was complete (TLC, 6−16 h), amine **16** (1.0 equiv) was added, followed by $Rh_2(OAc)_4$ (1 mol %), and the vial was sealed with a Teflon cap and heated to 80 °C (heating block) for 3 h. The reaction mixture was cooled to ambient temperature and boron trifluoride diethyl etherate (3.0 equiv) was added in one portion. The vial was sealed and heated to 80 °C (heating block) for 15 min. After being cooled to ambient temperature, the reaction was quenched by addition of saturated aqueous $NaHCO_3$, and the aqueous phase was extracted with CH_2Cl_2 (3 × 30 mL $mmol^{-1}$). The combined organic layers were washed with brine, dried ($MgSO_4$), filtered through a short pad of silica (eluting with CH_2Cl_2), and concentrated in vacuo to deliver the pyrrole **18**.

*3-Tosylamino-1,2,4-tri(4-tolyl)pyrrole (**18a**).* 1,2-Diaminoalkene **17a** (105 mg, 0.20 mmol, 1.0 equiv) was treated with $BF_3{\cdot}OEt_2$ (74 μL, 0.60 mmol, 3.0 equiv) in CH_2Cl_2 (6.7 mL) according to General Procedure 4 to give the title compound **18a** (74 mg, 73%) as an orange solid. 4-Ethynyltoluene (64 μL, 0.55 mmol, 1.1 equiv) and 4-toluenesulfonyl azide (108 mg, 0.55 mmol, 1.1 equiv) were treated with CuTC (5 mg, 26 μmol, 5 mol %) in CH_2Cl_2 (17 mL), followed by α-aminoketone **16a** (120 mg, 0.50 mmol, 1.0 equiv) and $Rh_2(OAc)_4$ (2 mg, 4.5 μmol, 1 mol %), and finally $BF_3{\cdot}OEt_2$ (185 μL, 1.5 mmol, 3.0 equiv) according to General Procedure 5 to give the title compound **18a** (228 mg, 90%): mp 170 °C dec; ν_{max} (film) 3268, 3028, 1516, 1389, 1327, and 1157 cm^{-1}; ^1H NMR (500 MHz, 25.0 °C, $CDCl_3$) δ 7.35 (2 H, d, J = 8.1 Hz, Ar), 7.25 (2 H, d, J = 8.0 Hz, Ar), 7.09 (2 H, d, J = 8.1 Hz, Ar), 7.07 (2 H, d, J = 8.4 Hz, Ar), 6.97 (2 H, d, J = 8.4 Hz, Ar), 6.94 (2 H, d, J = 8.1 Hz, Ar), 6.88 (1 H, s, pyrrole CH), 6.87 (2 H, d, J = 8.1 Hz, Ar), 6.82 (2 H, d, J = 8.0 Hz, Ar), 6.24 (1 H, s, NH), 2.37 (3 H, s, CH_3), 2.33 (3 H, s, CH_3), 2.32 (3 H, s, CH_3) and 2.30 (3 H, s, CH_3); $^{13}C\{^1H\}$ NMR (126 MHz, 25.0 °C, $CDCl_3$) δ 142.3 (Ar), 137.4 (Ar), 137.0 (Ar), 136.7 (Ar), 136.4 (Ar), 135.5 (Ar), 131.9 (Ar), 131.0 (Ar), 129.8 (2 × ArH), 129.5 (2 × ArH), 129.0 (2 × ArH), 128.7 (2 × ArH), 128.6 (2 × ArH), 127.4 (2 × ArH), 127.2 (pyrrole), 127.0 (2 × ArH), 125.2 (2 × ArH), 123.6 (pyrrole), 119.3 (pyrrole CH), 115.3 (pyrrole), 21.3 (CH_3), 21.3 (CH_3), 21.2 (CH_3) and 21.2 (CH_3); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{32}H_{31}N_2O_2S^+$ 507.2101; found 507.2100.

*1-(4-Chlorophenyl)-2,4-di(4-tolyl)-3-tosylaminopyrrole (**18b**).* 1,2-Diaminoalkene **17b** (109 mg, 0.20 mmol, 1.0 equiv) was treated with $BF_3{\cdot}OEt_2$ (74 μL, 0.60 mmol, 3.0 equiv) in CH_2Cl_2 (6.7 mL) according to General Procedure 4 to give the title compound **18b** (86 mg, 82%) as a yellow solid. 4-Ethynyltoluene (38 μL, 0.33 mmol, 1.1 equiv) and 4-toluenesulfonyl azide (66 mg, 0.33 mmol, 1.1 equiv) were treated with CuTC (3 mg, 16 μmol, 5 mol %) in CH_2Cl_2 (10 mL), followed by α-aminoketone **16b** (78 mg, 0.30 mmol, 1.0 equiv) and $Rh_2(OAc)_4$ (1 mg, 2.3 μmol, 1 mol %), and finally $BF_3{\cdot}OEt_2$ (111 μL, 0.90 mmol, 3.0 equiv) according to General Procedure 5 to give the title compound **18b** (101 mg, 64%): mp 170 °C dec; ν_{max} (film) 3268, 3020, 2920, 1497, 1385, 1327, 1157, and 1092 cm^{-1}; ^1H NMR (400 MHz, 25.0 °C, $CDCl_3$) δ 7.31 (2 H, d, J = 8.0 Hz, Ar), 7.22 (2 H, d, J = 8.0 Hz, Ar), 7.21 (2 H, d, J = 8.7 Hz, Ar), 7.07 (2 H, d, J = 8.0 Hz, Ar), 6.99 (2 H, d, J = 8.7 Hz, Ar), 6.94 (2 H, d, J = 7.9 Hz, Ar), 6.85 (1 H, s, pyrrole CH), 6.84 (2 H, d, J = 7.9 Hz, Ar), 6.81 (2 H, d, J = 8.0 Hz, Ar), 6.19 (1 H, s, NH), 2.35 (3 H, s, CH_3), 2.31 (3 H, s, CH_3) and 2.28 (3 H, s, CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, 23.0 °C, $CDCl_3$) δ 142.4 (Ar), 138.4 (Ar), 137.1 (Ar), 137.0 (Ar), 135.8 (Ar), 132.3 (Ar), 130.7 (Ar), 129.9 (2 × ArH), 129.3 (Ar), 129.1 (2 × ArH), 129.0 (2 × ArH), 128.9 (2 × ArH), 128.7 (2 × ArH), 127.4 (2 × ArH), 127.0 (2 × ArH), 126.8 (pyrrole), 126.5 (2 × ArH), 124.2 (pyrrole), 119.1 (pyrrole CH), 115.9 (pyrrole), 21.4 (CH_3), 21.3 (CH_3) and 21.2 (CH_3); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{31}H_{28}ClN_2O_2S^+$ 527.1555; found 527.1562.

*2,4-Di(4-tolyl)-3-tosyl-1-(3-trifluoromethylphenyl)aminopyrrole (**18c**).* 1,2-Diaminoalkene **17c** (58 mg, 0.10 mmol, 1.0 equiv) was treated with $BF_3{\cdot}OEt_2$ (37 μL, 0.30 mmol, 3.0 equiv) in CH_2Cl_2 (3.3 mL) according to General Procedure 4 to give the title compound **18c** (36 mg, 64%) as a yellow solid. 4-Ethynyltoluene (38 μL, 0.33 mmol, 1.1 equiv) and 4-toluenesulfonyl azide (66 mg, 0.33 mmol, 1.1 equiv) were treated with CuTC (3 mg, 16 μmol, 5 mol %) in CH_2Cl_2 (10 mL), followed by α-aminoketone **16c** (88 mg, 0.30 mmol, 1.0 equiv) and $Rh_2(OAc)_4$ (1 mg, 2.3 μmol, 1 mol %), and finally $BF_3{\cdot}OEt_2$ (111 μL, 0.90 mmol, 3.0 equiv) according to General Procedure 5 to give the title compound **18c** (131 mg, 78%): mp 145 °C dec; ν_{max} (film) 3256, 2924, 1497, 1458, 1385, 1327, 1161, 1130, 1096, and 1072 cm^{-1}; ^1H NMR (400 MHz, 25.0 °C, $CDCl_3$) δ 7.48−7.43 (1 H, m, Ar), 7.40−7.37 (1 H, m, Ar), 7.35 (1 H, d, J = 7.8 Hz, Ar), 7.31 (2 H, d, J = 7.9 Hz, Ar), 7.23 (2 H, d, J = 8.2 Hz, Ar), 7.17−7.13 (1 H, m, Ar), 7.07 (2 H, d, J = 7.9 Hz, Ar), 6.95 (2 H, d, J = 8.0 Hz, Ar), 6.91 (1 H, s, pyrrole CH), 6.84 (2 H, d, J = 8.0 Hz, Ar), 6.82 (2 H, d, J = 8.2 Hz, Ar), 6.20 (1 H, s, NH), 2.35 (3 H, s, CH_3), 2.30 (3 H, s, CH_3) and 2.28 (3 H, s, CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, 25.0 °C, $CDCl_3$) δ 142.5 (Ar), 140.3 (Ar), 137.4 (Ar), 136.9 (Ar), 135.9 (Ar), 132.1 (Ar), 131.5 (q, J = 32.9 Hz, Ar), 130.5 (Ar), 129.9 (2 × ArH), 129.4 (ArH), 129.0 (2 × ArH), 129.0 (2 × ArH), 128.7 (2 × ArH), 128.6 (ArH), 127.5 (2 × ArH), 127.0 (2 × ArH), 126.6 (pyrrole), 124.6 (pyrrole), 123.5 (q, J = 272.4 Hz, CF_3), 123.2 (q, J = 3.8 Hz, ArH), 121.9 (q, J = 3.5 Hz, ArH), 118.9 (pyrrole CH), 116.4 (pyrrole), 21.4 (CH_3), 21.3 (CH_3) and 21.2 (CH_3); HRMS (ESI-

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TOF) m/z $[M + H]^+$ calcd for $C_{32}H_{28}F_3N_2O_2S^+$ 561.1818; found 561.1826.

*2,4-Di(4-tolyl)-1-(4-methoxyphenyl)-3-tosylaminopyrrole (**18d**).* 1,2-Diaminoalkene **17d** (108 mg, 0.20 mmol, 1.0 equiv) was treated with $BF_3{\cdot}OEt_2$ (74 μL, 0.60 mmol, 3.0 equiv) in CH_2Cl_2 (6.7 mL) according to General Procedure 4 to give the title compound **18d** (69 mg, 66%) as a yellow solid: mp 158 °C dec; ν_{max} (film) 3271, 2920, 2859, 1512, 1323, 1250, 1157, 1092, and 1034 cm^{-1}; ^1H NMR (400 MHz, 22.1 °C, $CDCl_3$) δ 7.33 (2 H, d, J = 8.0 Hz, Ar), 7.23 (2 H, d, J = 8.2 Hz, Ar), 7.06 (2 H, d, J = 8.0 Hz, Ar), 6.99 (2 H, d, J = 9.0 Hz, Ar), 6.91 (2 H, d, J = 7.8 Hz, Ar), 6.84 (2 H, d, J = 7.8 Hz, Ar), 6.83 (1 H, s, pyrrole CH), 6.80 (2 H, d, J = 8.2 Hz, Ar), 6.77 (2 H, d, J = 9.0 Hz, Ar), 6.23 (1 H, s, NH), 3.77 (3 H, s, OCH_3), 2.34 (3 H, s, CH_3), 2.29 (3 H, s, CH_3) and 2.27 (3 H, s, CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, 22.9 °C, $CDCl_3$) δ 158.1 (Ar), 142.3 (Ar), 137.0 (Ar), 136.7 (Ar), 135.5 (Ar), 133.0 (Ar), 132.1 (Ar), 131.1 (Ar), 129.9 (2 × ArH), 128.9 (2 × ArH), 128.7 (2 × ArH), 128.6 (2 × ArH), 127.4 (2 × ArH), 127.2 (pyrrole), 127.0 (2 × ArH), 126.7 (2 × ArH), 123.4 (pyrrole), 119.5 (pyrrole CH), 115.0 (pyrrole), 114.0 (2 × ArH), 55.4 (OCH_3), 21.4 (CH_3), 21.3 (CH_3) and 21.2 (CH_3); HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{32}H_{30}N_2NaO_3S^+$ 545.1869; found 545.1858.

*2,4-Di(4-tolyl)-3-tosyl-1-(2,4,6-trimethylphenyl)aminopyrrole (**18e**).* Triazole **4a** (94 mg, 0.30 mmol, 1.0 equiv) and α-aminoketone **16e** (88 mg, 0.33 mmol, 1.1 equiv) were treated with $Rh_2(OAc)_4$ (7 mg, 0.02 mmol, 5 mol %) in PhMe (10 mL) according to General Procedure 3. During the N−H insertion, spontaneous cyclodehydration occurred to give the title compound **18e** (111 mg, 69%) as a yellow wax: ν_{max} (film) 3264, 3024, 2920, 2866, 1493, 1381, 1327, and 1161 cm^{-1}; ^1H NMR (400 MHz, 25.0 °C, $CDCl_3$) δ 7.35 (2 H, d, J = 8.0 Hz, Ar), 7.19 (2 H, d, J = 8.3 Hz, Ar), 7.09 (2 H, d, J = 8.0 Hz, Ar), 6.84 (2 H, d, J = 8.0 Hz, Ar), 6.81 (2 H, s, Ar), 6.80 (2 H, d, J = 8.3 Hz, Ar), 6.69 (2 H, d, J = 8.0 Hz, Ar), 6.57 (1 H, s, pyrrole CH), 6.27 (1 H, s, NH), 2.35 (3 H, s, CH_3), 2.28 (3 H, s, CH_3), 2.25 (3 H, s, CH_3), 2.24 (3 H, s, CH_3) and 1.92 (6 H, s, 2 × CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, 25.0 °C, $CDCl_3$) δ 142.5 (Ar), 137.9 (Ar), 136.5 (Ar), 136.0 (Ar), 135.7 (2 × Ar), 135.6 (Ar), 135.4 (Ar), 132.0 (Ar), 131.3 (Ar), 128.9 (2 × ArH), 128.7 (2 × ArH), 128.6 (2 × ArH), 128.5 (4 × ArH), 127.3 (pyrrole), 127.3 (2 × ArH), 127.2 (2 × ArH), 123.4 (pyrrole), 118.6 (pyrrole CH), 113.7 (pyrrole), 21.5 (CH_3), 21.2 (CH_3), 21.2 (CH_3), 21.0 (CH_3) and 17.7 (2 × CH_3); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{34}H_{35}N_2O_2S^+$ 535.2414; found 535.2423.

*2,4-Di(4-tolyl)-1-naphth-2-yl-3-tosylaminopyrrole (**18f**).* Triazole **4a** (94 mg, 0.30 mmol, 1.0 equiv) and α-aminoketone **16f** (91 mg, 0.33 mmol, 1.1 equiv) were treated with $Rh_2(OAc)_4$ (7 mg, 0.02 mmol, 5 mol %) in PhMe (10 mL) according to General Procedure 3. During the N−H insertion, spontaneous cyclodehydration occurred to give the title compound **18f** (117 mg, 72%) as a yellow solid: mp 150 °C dec; ν_{max} (film) 3268, 3048, 2920, 2866, 1412, 1323, 1157, and 1092 cm^{-1}; ^1H NMR (400 MHz, 25.0 °C, $CDCl_3$) δ 7.88−7.83 (1 H, m, naphthyl CH), 7.79 (1 H, d, J = 8.4 Hz, naphthyl CH), 7.62−7.58 (1 H, m, naphthyl CH), 7.55−7.45 (2 H, m, naphthyl CH), 7.40 (2 H, d, J = 8.1 Hz, Ar), 7.34 (1 H, dd, J = 8.3, 7.3 Hz, naphthyl CH), 7.28 (2 H, d, J = 8.4 Hz, Ar), 7.21 (1 H, dd, J = 7.3, 1.2 Hz, naphthyl CH), 7.10 (2 H, d, J = 7.6 Hz, Ar), 6.89 (1 H, s, pyrrole CH), 6.83 (2 H, d, J = 7.6 Hz, Ar), 6.73 (4 H, app s, Ar), 6.29 (1 H, s, NH), 2.36 (3 H, s, CH_3), 2.27 (3 H, s, CH_3) and 2.16 (3 H, s, CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, 25.0 °C, $CDCl_3$) δ 142.5 (naphthyl C), 136.7 (Ar), 136.6 (Ar), 136.4 (Ar), 135.6 (Ar), 134.0 (naphthyl C), 133.8 (pyrrole), 131.0 (Ar), 130.8 (naphthyl C), 129.2 (2 × ArH), 129.0 (2 × ArH), 128.7 (2 × ArH), 128.5 (2 × ArH), 128.4 (naphthyl CH), 128.1 (naphthyl CH), 127.4 (2 × ArH), 127.2 (2 × ArH), 127.1 (Ar), 127.0 (naphthyl CH), 126.5 (naphthyl CH), 125.7 (naphthyl CH), 125.0 (naphthyl CH), 123.3 (pyrrole), 123.1 (naphthyl CH), 121.1 (pyrrole CH), 114.6 (pyrrole), 21.4 (CH_3), 21.2 (CH_3) and 21.1 (CH_3); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{35}H_{31}N_2O_2S^+$ 543.2101; found 543.2109.

*5-Methyl-3-tosylamino-1,2,4-tri(4-tolyl)pyrrole (**18g**).* 1,2-Diaminoalkene **17g** (54 mg, 0.10 mmol, 1.0 equiv) was treated with $BF_3{\cdot}OEt_2$ (37 μL, 0.30 mmol, 3.0 equiv) in CH_2Cl_2 (3.3 mL) according to General Procedure 4 to give the title compound **18g** (38 mg, 73%) as a yellow solid. 4-Ethynyltoluene (38 μL, 0.33 mmol, 1.1 equiv) and 4-toluenesulfonyl azide (66 mg, 0.33 mmol, 1.1 equiv) were treated with CuTC (3 mg, 16 μmol, 5 mol %) in CH_2Cl_2 (10 mL), followed by α-aminoketone **16g** (76 mg, 0.30 mmol, 1.0 equiv) and $Rh_2(OAc)_4$ (1 mg, 2.3 μmol, 1 mol %), and finally $BF_3{\cdot}OEt_2$ (111 μL, 0.90 mmol, 3.0 equiv) according to General Procedure 5 to give the title compound **18g** (106 mg, 68%): mp 154 °C dec; ν_{max} (film) 3271, 3028, 2920, 2866, 1512, 1381, 1323, 1157, and 1092 cm^{-1}; ^1H NMR (400 MHz, 25.0 °C, $CDCl_3$) δ 7.19 (2 H, d, J = 8.3 Hz, Ar), 7.14−7.06 (6 H, m, Ar), 6.98 (2 H, d, J = 8.3 Hz, Ar), 6.86−6.84 (4 H, m, Ar), 6.81 (2 H, d, J = 7.9 Hz, Ar), 6.18 (1 H, s, NH), 2.37 (3 H, s, CH_3), 2.32 (3 H, s, CH_3), 2.29 (3 H, s, CH_3), 2.25 (3 H, s, CH_3) and 2.01 (3 H, s, CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, 25.0 °C, $CDCl_3$) δ 142.0 (Ar), 137.2 (Ar), 137.2 (Ar), 136.0 (Ar), 135.9 (Ar), 135.2 (Ar), 131.4 (Ar), 131.0 (Ar), 129.8 (2 × ArH), 129.6 (2 × ArH), 129.4 (2 × ArH), 128.8 (2 × ArH), 128.6 (2 × ArH), 128.4 (2 × ArH), 128.3 (2 × ArH), 127.9 (pyrrole), 126.9 (2 × ArH), 125.9 (pyrrole), 120.6 (pyrrole), 114.6 (pyrrole), 21.4 (CH_3), 21.2 (CH_3), 21.2 (CH_3), 21.1 (CH_3) and 12.0 (CH_3); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{33}H_{33}N_2O_2S^+$ 521.2257; found 521.2256.

*1,2-Di(4-tolyl)-4-(naphth-2-yl)-3-tosylaminopyrrole (**18h**).* 1,2-Diaminoalkene **17h** (56 mg, 0.10 mmol, 1.0 equiv) was treated with $BF_3{\cdot}OEt_2$ (37 μL, 0.30 mmol, 3.0 equiv) in CH_2Cl_2 (3.3 mL) according to General Procedure 4 to give the title compound **18h** (36 mg, 66%) as an orange solid. 4-Ethynyltoluene (38 μL, 0.33 mmol, 1.3 equiv) and 4-toluenesulfonyl azide (66 mg, 0.33 mmol, 1.3 equiv) were treated with CuTC (3 mg, 16 μmol, 6 mol %) in CH_2Cl_2 (10 mL), followed by α-aminoketone **16h** (72 mg, 0.26 mmol, 1.0 equiv) and $Rh_2(OAc)_4$ (1 mg, 2.3 μmol, 1 mol %), and finally $BF_3{\cdot}OEt_2$ (111 μL, 0.90 mmol, 3.4 equiv) according to General Procedure 5 to give the title compound **18h** (142 mg, > 98%). On a larger scale, 4-ethynyltoluene (590 μL, 5.1 mmol, 1.1 equiv) and 4-toluenesulfonyl azide (1.29 g, 6.5 mmol, 1.4 equiv) were treated with CuTC (44 mg, 0.23 mmol, 5 mol %) in CH_2Cl_2 (170 mL), followed by α-aminoketone **16h** (1.27 g, 4.6 mmol, 1.0 equiv) and $Rh_2(OAc)_4$ (20 mg, 45 μmol, 1 mol %), and finally $BF_3{\cdot}OEt_2$ (1.71 mL, 14 mmol, 3.0 equiv) according to General Procedure 5 to give the title compound (1.89 g, 76%) as an orange solid: mp 160 °C dec; ν_{max} (film) 3264, 3036, 2924, 1516, 1377, 1327, 1157, and 1092 cm^{-1}; ^1H NMR (400 MHz, 25.0 °C, $CDCl_3$) δ 7.79−7.76 (2 H, m, Ar), 7.73−7.69 (1 H, m, Ar), 7.67 (1 H, d, J = 8.5 Hz, Ar), 7.52 (1 H, dd, J = 8.4, 1.7 Hz, Ar), 7.47−7.39 (2 H, m, Ar), 7.21 (2 H, d, J = 8.3 Hz, Ar), 7.08 (2 H, d, J = 7.9 Hz, Ar), 7.02−6.98 (6 H, m, Ar), 7.00 (1 H, s, pyrrole CH), 6.57 (2 H, d, J = 7.8 Hz, Ar), 6.27 (1 H, s, NH), 2.33 (3 H, s, CH_3), 2.32 (3 H, s, CH_3) and 1.98 (3 H, s, CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, 25.0 °C, $CDCl_3$) δ 142.5 (Ar), 137.4 (Ar), 137.0 (Ar), 136.9 (Ar), 136.6 (Ar), 133.6 (naphthyl C), 132.7 (Ar), 132.0 (naphthyl C), 131.5 (naphthyl C), 130.0 (2 × ArH), 129.5 (2 × ArH), 128.8 (2 × ArH), 128.6 (2 × ArH), 127.9 (naphthyl CH), 127.7 (naphthyl CH), 127.5 (naphthyl CH), 127.2 (naphthyl CH), 126.9 (2 × ArH), 126.3 (naphthyl CH), 125.7 (pyrrole), 125.6 (naphthyl CH), 125.3 (2 × ArH), 125.2 (naphthyl CH), 123.4 (pyrrole), 119.9 (pyrrole CH), 115.5 (pyrrole), 21.3 (CH_3), 21.1 (CH_3) and 21.0 (CH_3); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{35}H_{31}N_2O_2S^+$ 543.2101; found 543.2109.

*1,2-Di(4-tolyl)-4-(4-methoxyphenyl)-3-tosylaminopyrrole (**18i**).* 1,2-Diaminoalkene **17i** (54 mg, 0.10 mmol, 1.0 equiv) was treated with $BF_3{\cdot}OEt_2$ (37 μL, 0.30 mmol, 3.0 equiv) in CH_2Cl_2 (3.3 mL) according to General Procedure 4 to give the title compound **18i** (32 mg, 61%) as a yellow solid: mp 160 °C dec; ν_{max} (film) 3264, 3036, 2920, 2859, 1505, 1389, 1323, 1242, 1157, and 1092 cm^{-1}; ^1H NMR (400 MHz, 26.0 °C, $CDCl_3$) δ 7.36 (2 H, d, J = 8.8 Hz, Ar), 7.24 (2 H, d, J = 8.4 Hz, Ar), 7.04 (2 H, d, J = 7.9 Hz, Ar), 6.94 (2 H, d, J = 8.2 Hz, Ar), 6.91 (2 H, d, J = 8.2 Hz, Ar), 6.84 (2 H, d, J = 7.9 Hz, Ar), 6.83 (1 H, s, pyrrole CH), 6.82 (2 H, d, J = 8.4 Hz, Ar), 6.80 (2 H, d, J = 8.8 Hz, Ar), 6.17 (1 H, s, NH), 3.82 (3 H, s, OCH_3), 2.30 (3 H, s, CH_3), 2.29 (3 H, s, CH_3) and 2.28 (3 H, s, CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, 26.0 °C, $CDCl_3$) δ 158.1 (Ar), 142.4 (Ar), 137.4

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(Ar), 137.1 (Ar), 136.8 (Ar), 136.4 (Ar), 131.8 (Ar), 129.9 (2 × ArH), 129.5 (2 × ArH), 128.7 (2 × ArH), 128.7 (2 × ArH), 128.6 (2 × ArH), 127.3 (Ar), 127.1 (2 × ArH), 126.6 (pyrrole), 125.2 (2 × ArH), 123.3 (pyrrole), 119.1 (pyrrole CH), 115.3 (pyrrole), 113.7 (2 × ArH), 55.2 (OCH_3), 21.4 (CH_3), 21.3 (CH_3) and 20.9 (CH_3); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{32}H_{31}N_2O_3S^+$ 523.2050; found 523.2059.

*1,2-Di(4-tolyl)-4-(4-nitrophenyl)-3-tosylaminopyrrole (**18j**).* 1,2-Diaminoalkene **17j** (56 mg, 0.10 mmol, 1.0 equiv) was treated with $BF_3{\cdot}OEt_2$ (37 μL, 0.30 mmol, 3.0 equiv) in CH_2Cl_2 (3.3 mL) according to General Procedure 4 to give the title compound **18j** (42 mg, 78%) as an orange solid. 4-Ethynyltoluene (38 μL, 0.33 mmol, 1.1 equiv) and 4-toluenesulfonyl azide (66 mg, 0.33 mmol, 1.1 equiv) were treated with CuTC (3 mg, 16 μmol, 5 mol %) in CH_2Cl_2 (10 mL), followed by α-aminoketone **16j** (81 mg, 0.30 mmol, 1.0 equiv) and $Rh_2(OAc)_4$ (1 mg, 2.3 μmol, 1 mol %), and finally $BF_3{\cdot}OEt_2$ (111 μL, 0.90 mmol, 3.0 equiv) according to General Procedure 5 to give the title compound **18j** (120 mg, 74%): mp 175 °C dec; ν_{max} (film) 3264, 3036, 2924, 1597, 1393, 1335, 1161, and 1151 cm^{-1}; ^1H NMR (400 MHz, 25.0 °C, $CDCl_3$) δ 8.11 (2 H, d, J = 8.9 Hz, Ar), 7.71 (2 H, d, J = 8.9 Hz, Ar), 7.23 (2 H, d, J = 8.3 Hz, Ar), 7.07 (2 H, d, J = 8.1 Hz, Ar), 7.04 (1 H, s, pyrrole CH), 6.96−6.90 (4 H, m, Ar), 6.83 (2 H, d, J = 8.3 Hz, Ar), 6.74 (2 H, d, J = 8.1 Hz, Ar), 6.32 (1 H, s, NH), 2.31 (3 H, s, CH_3), 2.30 (3 H, s, CH_3) and 2.25 (3 H, s, CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, 25.0 °C, $CDCl_3$) δ 145.6 (Ar), 143.1 (Ar), 141.4 (Ar), 137.4 (Ar), 137.2 (Ar), 136.8 (Ar), 136.5 (Ar), 132.9 (Ar), 129.7 (2 × ArH), 129.6 (2 × ArH), 128.9 (2 × ArH), 128.9 (2 × ArH), 127.4 (2 × ArH), 127.1 (2 × ArH), 126.3 (pyrrole), 125.1 (2 × ArH), 123.7 (2 × ArH), 121.3 (pyrrole), 120.8 (pyrrole CH), 115.4 (pyrrole), 21.3 (CH_3), 21.3 (CH_3) and 21.0 (CH_3); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{31}H_{28}N_3O_4S^+$ 538.1795; found 538.1803.

*4-(4-Cyanophenyl)-1,2-di(4-tolyl)-3-tosylaminopyrrole (**18k**).* 1,2-Diaminoalkene **17k** (54 mg, 0.10 mmol, 1.0 equiv) was treated with $BF_3{\cdot}OEt_2$ (37 μL, 0.30 mmol, 3.0 equiv) in CH_2Cl_2 (3.3 mL) according to General Procedure 4 to give the title compound **18k** (37 mg, 71%) as a yellow solid: mp 165 °C dec; ν_{max} (film) 3275, 3036, 2924, 2226, 1605, 1543, 1516, 1393, 1327, and 1161 cm^{-1}; ^1H NMR (400 MHz, 25.0 °C, $CDCl_3$) δ 7.65 (2 H, d, J = 8.7 Hz, Ar), 7.52 (2 H, d, J = 8.7 Hz, Ar), 7.22 (2 H, d, J = 8.1 Hz, Ar), 7.06 (2 H, d, J = 7.9 Hz, Ar), 6.99 (1 H, s, pyrrole CH), 6.95−6.90 (4 H, m, Ar), 6.84 (2 H, d, J = 8.1 Hz, Ar), 6.74 (2 H, d, J = 8.1 Hz, Ar), 6.27 (1 H, s, NH), 2.31 (3 H, s, CH_3), 2.30 (3 H, s, CH_3) and 2.30 (3 H, s, CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, 25.0 °C, $CDCl_3$) δ 143.0 (Ar), 139.2 (Ar), 137.3 (Ar), 137.1 (Ar), 136.9 (Ar), 136.5 (Ar), 132.8 (Ar), 132.0 (2 × ArH), 129.7 (2 × ArH), 129.6 (2 × ArH), 128.9 (2 × ArH), 128.9 (2 × ArH), 127.5 (2 × ArH), 127.0 (2 × ArH), 126.4 (pyrrole), 125.1 (2 × ArH), 121.7 (pyrrole), 120.5 (pyrrole CH), 119.4 (pyrrole), 115.3 (C≡N), 109.0 (Ar), 21.4 (CH_3), 21.3 (CH_3) and 21.0 (CH_3); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{32}H_{28}N_3O_2S^+$ 518.1897; found 518.1904.

*4-(4-Chlorophenyl)-1,2-di(4-tolyl)-3-tosylaminopyrrole (**18l**).* 1,2-Diaminoalkene **17l** (55 mg, 0.10 mmol, 1.0 equiv) was treated with $BF_3{\cdot}OEt_2$ (37 μL, 0.30 mmol, 3.0 equiv) in CH_2Cl_2 (3.3 mL) according to General Procedure 4 to give the title compound **18l** (41 mg, 77%) as a yellow solid: mp 160 °C dec; ν_{max} (film) 3268, 2924, 1501, 1389, 1157, and 1092 cm^{-1}; ^1H NMR (400 MHz, 26.0 °C, $CDCl_3$) δ 7.36 (2 H, d, J = 8.5 Hz, Ar), 7.24 (2 H, d, J = 8.3 Hz, Ar), 7.18 (2 H, d, J = 8.5 Hz, Ar), 7.05 (2 H, d, J = 8.0 Hz, Ar), 6.95 (2 H, d, J = 8.1 Hz, Ar), 6.93 (2 H, d, J = 8.3 Hz, Ar), 6.88 (1 H, s, pyrrole CH), 6.85 (2 H, d, J = 8.1 Hz, Ar), 6.84 (2 H, d, J = 8.0 Hz, Ar), 6.18 (1 H, s, NH), 2.31 (6 H, s, 2 × CH_3) and 2.30 (3 H, s, CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, 26.0 °C, $CDCl_3$) δ 142.8 (Ar), 137.2 (Ar), 137.1 (Ar), 136.9 (Ar), 136.7 (Ar), 132.6 (Ar), 132.4 (Ar), 131.8 (Ar), 129.9 (2 × ArH), 129.5 (2 × ArH), 128.8 (2 × ArH), 128.8 (2 × ArH), 128.6 (2 × ArH), 128.3 (2 × ArH), 127.0 (2 × ArH), 126.9 (pyrrole), 125.2 (2 × ArH), 122.4 (pyrrole), 119.6 (pyrrole CH), 115.2 (pyrrole), 21.5 (CH_3), 21.3 (CH_3) and 21.0 (CH_3); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{31}H_{28}ClN_2O_2S^+$ 527.1555; found 527.1559.

*1,4-Di(4-tolyl)-2-(thiophen-2-yl)-3-tosylaminopyrrole (**18m**).* 1,2-Diaminoalkene **17m** (52 mg, 0.10 mmol, 1.0 equiv) was treated with $BF_3{\cdot}OEt_2$ (37 μL, 0.30 mmol, 3.0 equiv) in CH_2Cl_2 (3.3 mL) according to General Procedure 4 to give the title compound **18m** (38 mg, 76%) as a yellow solid: mp 187 °C dec; ν_{max} (film) 3268, 2920, 1516, 1397, 1327, 1161, and 1092 cm^{-1}; ^1H NMR (400 MHz, 25.0 °C, $CDCl_3$) δ 7.32 (2 H, d, J = 8.3 Hz, Ar), 7.24 (2 H, d, J = 8.1 Hz, Ar), 7.18 (1 H, dd, J = 5.1, 1.2 Hz, thiophene CH), 7.12 (2 H, d, J = 8.2 Hz, Ar), 7.05 (2 H, d, J = 8.2 Hz, Ar), 7.03 (2 H, d, J = 8.1 Hz, Ar), 6.86 (2 H, d, J = 8.3 Hz, Ar), 6.85 (1 H, s, pyrrole CH), 6.82 (1 H, dd, J = 5.1, 3.6 Hz, thiophene CH), 6.66 (1 H, dd, J = 3.6, 1.2 Hz, thiophene CH), 6.32 (1 H, s, NH), 2.35 (3 H, s, CH_3), 2.34 (3 H, s, CH_3) and 2.28 (3 H, s, CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, 25.0 °C, $CDCl_3$) δ 142.5 (Ar), 137.3 (Ar), 137.1 (Ar), 136.9 (Ar), 135.6 (Ar), 130.7 (Ar), 130.7 (thiophene C2), 129.5 (2 × ArH), 128.9 (2 × ArH), 128.8 (2 × ArH), 128.4 (thiophene CH), 127.3 (2 × ArH), 127.1 (2 × ArH), 126.7 (thiophene CH), 126.4 (thiophene CH), 125.7 (2 × ArH), 125.6 (pyrrole), 123.6 (pyrrole), 120.4 (pyrrole CH), 116.5 (pyrrole), 21.4 (CH_3), 21.2 (CH_3) and 21.0 (CH_3); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{29}H_{27}N_2O_2S_2^+$ 499.1508; found 499.1517.

*1,4-Di(4-tolyl)-2-(4-methoxyphenyl)-3-tosylaminopyrrole (**18n**).* 1,2-Diaminoalkene **17n** (54 mg, 0.10 mmol, 1.0 equiv) was treated with $BF_3{\cdot}OEt_2$ (37 μL, 0.30 mmol, 3.0 equiv) in CH_2Cl_2 (3.3 mL) according to General Procedure 4 to give the title compound **18n** (44 mg, 84%) as a yellow solid: mp 75 °C dec; ν_{max} (film) 3275, 2924, 1516, 1393, 1323, 1250, 1157, and 1092 cm^{-1}; ^1H NMR (400 MHz, 25.0 °C, $CDCl_3$) δ 7.31 (2 H, d, J = 8.1 Hz, Ar), 7.24 (2 H, d, J = 8.3 Hz, Ar), 7.06 (2 H, d, J = 8.1 Hz, Ar), 7.05 (2 H, d, J = 8.3 Hz, Ar), 6.94 (2 H, d, J = 8.4 Hz, Ar), 6.90 (2 H, d, J = 8.8 Hz, Ar), 6.85 (1 H, s, pyrrole CH), 6.82 (2 H, d, J = 8.4 Hz, Ar), 6.65 (2 H, d, J = 8.8 Hz, Ar), 6.15 (1 H, s, NH), 3.78 (3 H, s, OCH_3), 2.34 (3 H, s, CH_3), 2.31 (3 H, s, CH_3) and 2.27 (3 H, s, CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, 25.0 °C, $CDCl_3$) δ 158.7 (Ar), 142.4 (Ar), 137.4 (Ar), 137.1 (Ar), 136.5 (Ar), 135.5 (Ar), 131.8 (Ar), 131.3 (2 × ArH), 131.1 (Ar), 129.5 (2 × ArH), 129.0 (2 × ArH), 128.7 (2 × ArH), 127.4 (2 × ArH), 127.1 (2 × ArH), 125.3 (2 × ArH), 123.5 (pyrrole), 122.7 (pyrrole), 119.2 (pyrrole CH), 115.2 (pyrrole), 113.5 (2 × ArH), 55.1 (OCH_3), 21.4 (CH_3), 21.2 (CH_3) and 21.0 (CH_3); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{32}H_{31}N_2O_3S^+$ 523.2050; found 523.2057.

*1,4-Di(4-tolyl)-2-(cyclohexen-1-yl)-3-tosylaminopyrrole (**18o**).* 1,2-Diaminoalkene **17o** (51 mg, 0.10 mmol, 1.0 equiv) was treated with $BF_3{\cdot}OEt_2$ (37 μL, 0.30 mmol, 3.0 equiv) in CH_2Cl_2 (3.3 mL) according to General Procedure 4 to give the title compound **18o** (28 mg, 57%) as a brown solid: mp 80 °C dec; ν_{max} (film) 3271, 3036, 2928, 1709, 1593, 1516, 1492, 1393, 1246, 1157, and 1092 cm^{-1}; ^1H NMR (400 MHz, 25.0 °C, $CDCl_3$) δ 7.41 (2 H, d, J = 8.3 Hz, Ar), 7.22 (2 H, d, J = 8.5 Hz, Ar), 7.19 (2 H, d, J = 8.5 Hz, Ar), 7.17 (2 H, d, J = 8.3 Hz, Ar), 7.00 (2 H, d, J = 7.9 Hz, Ar), 6.97 (2 H, d, J = 7.9 Hz, Ar), 6.69 (1 H, s, pyrrole CH), 6.15 (1 H, s, NH), 5.80−5.76 (1 H, m, =CH), 2.37 (3 H, s, CH_3), 2.32 (3 H, s, CH_3), 2.30 (3 H, s, CH_3), 2.10−2.03 (2 H, m, CH_2), 1.57−1.52 (2 H, m, CH_2), 1.48−1.42 (2 H, m, CH_2) and 1.39−1.32 (2 H, m, CH_2); $^{13}C\{^1H\}$ NMR (101 MHz, 25.0 °C, $CDCl_3$) δ 142.6 (Ar), 138.1 (Ar), 137.2 (Ar), 136.5 (Ar), 135.2 (Ar), 134.5 (pyrrole), 131.5 (=CH), 131.2 (Ar), 129.6 (2 × ArH), 128.9 (2 × ArH), 128.8 (2 × ArH), 128.7 (=C), 127.4 (2 × ArH), 127.2 (2 × ArH), 124.0 (2 × ArH), 123.0 (pyrrole), 118.1 (pyrrole CH), 114.4 (pyrrole), 28.2 (CH_2), 25.7 (CH_2), 22.4 (CH_2), 21.5 (CH_2), 21.4 (CH_3), 21.1 (CH_3) and 21.0 (CH_3); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{31}H_{33}N_2O_2S^+$ 497.2257; found 497.2265.

*3-(4-Methoxybenzenesulfonylamino)-1,2,4-tri(4-tolyl)pyrrole (**18p**).* 1,2-Diaminoalkene **17p** (54 mg, 0.10 mmol, 1.0 equiv) was treated with $BF_3{\cdot}OEt_2$ (37 μL, 0.30 mmol, 3.0 equiv) in CH_2Cl_2 (3.3 mL) according to General Procedure 4 to give the title compound **18p** (26 mg, 50%) as a yellow solid. 4-Ethynyltoluene (38 μL, 0.33 mmol, 1.1 equiv) and 4-methoxybenzenesulfonyl azide (70 mg, 0.33 mmol, 1.1 equiv) were treated with CuTC (3 mg, 16 μmol, 5 mol %) in CH_2Cl_2 (10 mL), followed by α-aminoketone **16a** (72 mg, 0.30

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mmol, 1.0 equiv) and $Rh_2(OAc)_4$ (1 mg, 2.3 μmol, 1 mol %), and finally $BF_3{\cdot}OEt_2$ (111 μL, 0.90 mmol, 3.0 equiv) according to General Procedure 5 to give the title compound **18p** (88 mg, 56%): mp 150 °C dec; ν_{max} (film) 3271, 3020, 2920, 1593, 1501, 1389, 1323, 1258, 1153, and 1096 cm^{-1}; ^1H NMR (400 MHz, 25.0 °C, $CDCl_3$) δ 7.33 (2 H, d, *J* = 8.2 Hz, Ar), 7.27 (2 H, d, *J* = 8.9 Hz, Ar), 7.06 (2 H, d, *J* = 7.7 Hz, Ar), 7.05 (2 H, d, *J* = 7.7 Hz, Ar), 6.95 (2 H, d, *J* = 8.9 Hz, Ar), 6.93 (2 H, d, *J* = 8.2 Hz, Ar), 6.87 (2 H, d, *J* = 9.1 Hz, Ar), 6.86 (1 H, s, pyrrole CH), 6.47 (2 H, d, *J* = 9.1 Hz, Ar), 6.17 (1 H, s, NH), 3.76 (3 H, s, OCH_3), 2.34 (3 H, s, CH_3), 2.31 (3 H, s, CH_3) and 2.29 (3 H, s, CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, 25.0 °C, $CDCl_3$) δ 162.3 (Ar), 137.4 (Ar), 136.7 (Ar), 136.5 (Ar), 135.5 (Ar), 131.9 (Ar), 131.6 (Ar), 131.1 (Ar), 129.9 (2 × ArH), 129.5 (2 × ArH), 129.1 (2 × ArH), 129.0 (2 × ArH), 128.8 (2 × ArH), 127.4 (2 × ArH), 127.3 (pyrrole), 125.2 (2 × ArH), 123.5 (pyrrole), 119.4 (pyrrole CH), 115.4 (pyrrole), 113.2 (2 × ArH), 55.3 (OCH_3), 21.2 (CH_3), 21.1 (CH_3) and 21.0 (CH_3); HRMS (ESI-TOF) *m*/*z* $[M + H]^+$ calcd for $C_{32}H_{31}N_2O_3S^+$ 523.2050; found 523.2058.

*3-(4-Nitrobenzenesulfonylamino)-1,2,4-tri(4-tolyl)pyrrole (**18q**).* 1,2-Diaminoalkene **17q** (56 mg, 0.10 mmol, 1.0 equiv) was treated with $BF_3{\cdot}OEt_2$ (37 μL, 0.30 mmol, 3.0 equiv) in CH_2Cl_2 (3.3 mL) according to General Procedure 4 to give the title compound **18q** (45 mg, 83%) as an orange solid: mp 180 °C dec; ν_{max} (film) 3271, 3036, 2920, 2862, 1516, 1404, 1389, 1346, 1161, and 1092 cm^{-1}; ^1H NMR (400 MHz, 25.0 °C, $CDCl_3$) δ 7.80 (2 H, d, *J* = 8.8 Hz, Ar), 7.53 (2 H, d, *J* = 8.8 Hz, Ar), 7.26 (2 H, d, *J* = 8.1 Hz, Ar), 7.06 (2 H, d, *J* = 7.6 Hz, Ar), 7.05 (2 H, d, *J* = 7.6 Hz, Ar), 6.94 (2 H, d, *J* = 8.3 Hz, Ar), 6.93 (2 H, d, *J* = 7.8 Hz, Ar), 6.88 (2 H, d, *J* = 8.3 Hz, Ar), 6.87 (1 H, s, pyrrole CH), 6.53 (1 H, s, NH), 2.32 (3 H, s, CH_3), 2.31 (3 H, s, CH_3) and 2.29 (3 H, s, CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, 25.0 °C, $CDCl_3$) δ 149.3 (Ar), 145.7 (Ar), 137.4 (Ar), 137.1 (Ar), 136.8 (Ar), 136.2 (Ar), 132.6 (Ar), 130.7 (Ar), 129.9 (2 × ArH), 129.6 (2 × ArH), 129.1 (2 × ArH), 128.9 (2 × ArH), 128.2 (2 × ArH), 127.4 (2 × ArH), 127.0 (pyrrole), 125.2 (2 × ArH), 123.7 (pyrrole), 123.2 (2 × ArH), 119.7 (pyrrole CH), 114.0 (pyrrole), 21.2 (CH_3), 21.0 (CH_3) and 21.0 (CH_3); HRMS (ESI-TOF) *m*/*z* $[M + H]^+$ calcd for $C_{31}H_{28}N_3O_4S^+$ 538.1795; found 538.1805.

*3-Mesylamino-1,2,4-tri(4-tolyl)pyrrole (**18r**).* 1,2-Diaminoalkene **17r** (45 mg, 0.10 mmol, 1.0 equiv) was treated with $BF_3{\cdot}OEt_2$ (37 μL, 0.30 mmol, 3.0 equiv) in CH_2Cl_2 (3.3 mL) according to General Procedure 4 to give the title compound **18r** (30 mg, 69%) as an orange solid: mp 93−94 °C; ν_{max} (film) 3268, 2924, 1516, 1393, 1319, and 1153 cm^{-1}; ^1H NMR (400 MHz, 25.0 °C, $CDCl_3$) δ 7.51 (2 H, d, *J* = 8.1 Hz, Ar), 7.22 (2 H, d, *J* = 7.8 Hz, Ar), 7.15 (2 H, d, *J* = 8.4 Hz, Ar), 7.10 (2 H, d, *J* = 8.1 Hz, Ar), 7.09 (2 H, d, *J* = 8.1 Hz, Ar), 7.02 (2 H, d, *J* = 8.4 Hz, Ar), 6.96 (1 H, s, pyrrole CH), 5.92 (1 H, s, NH), 2.37 (3 H, s, CH_3), 2.33 (3 H, s, CH_3), 2.32 (3 H, s, CH_3) and 2.29 (3 H, s, CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, 25.0 °C, $CDCl_3$) δ 137.5 (Ar), 137.4 (Ar), 136.7 (Ar), 136.3 (Ar), 132.1 (Ar), 131.0 (Ar), 130.2 (2 × ArH), 129.6 (2 × ArH), 129.5 (2 × ArH), 129.2 (2 × ArH), 127.9 (2 × ArH), 127.5 (pyrrole), 125.3 (2 × ArH), 123.7 (pyrrole), 119.5 (pyrrole CH), 115.3 (pyrrole), 40.7 (Ms), 21.3 (CH_3), 21.2 (CH_3) and 21.0 (CH_3); HRMS (ESI-TOF) *m*/*z* $[M + H]^+$ calcd for $C_{26}H_{27}N_2O_2S^+$ 431.1788; found 431.1797.

*4-(4-Cyanophenyl)-2-(4-methoxyphenyl)-1-(4-tolyl)-3-tosylaminopyrrole (**18s**).* 1-Ethynyl-4-methoxybenzene (43 μL, 0.32 mmol, 1.2 equiv) and 4-toluenesulfonyl azide (66 mg, 0.33 mmol, 1.2 equiv) were treated with CuTC (3 mg, 16 μmol, 6 mol %) in CH_2Cl_2 (10 mL), followed by α-aminoketone **16e** (75 mg, 0.28 mmol, 1.0 equiv) and $Rh_2(OAc)_4$ (1 mg, 2.3 μmol, 1 mol %), and finally $BF_3{\cdot}OEt_2$ (111 μL, 0.90 mmol, 3.2 equiv) according to General Procedure 5 to give the title compound **18s** (127 mg, 85%) as an orange solid: mp 140 °C dec; ν_{max} (film) 3268, 2924, 2226, 1609, 1566, 1516, 1327, 1292, 1250, 1161, 1092, and 1034 cm^{-1}; ^1H NMR (400 MHz, 25.0 °C, $CDCl_3$) δ 7.64 (2 H, d, *J* = 8.7 Hz, Ar), 7.52 (2 H, d, *J* = 8.7 Hz, Ar), 7.25 (2 H, d, *J* = 8.2 Hz, Ar), 7.06 (2 H, d, *J* = 7.9 Hz, Ar), 6.98 (1 H, s, pyrrole CH), 6.93 (2 H, d, *J* = 8.2 Hz, Ar), 6.86 (2 H, d, *J* = 7.9 Hz, Ar), 6.80 (2 H, d, *J* = 8.8 Hz, Ar), 6.65 (2 H, d, *J* = 8.8 Hz, Ar), 6.25 (1 H, s, NH), 3.78 (3 H, s, CH_3), 2.31 (3 H, s, CH_3) and 2.31 (3 H, s, CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, 25.0 °C, $CDCl_3$) δ 159.0 (Ar), 143.0 (Ar), 139.2 (Ar), 137.1 (Ar), 136.9 (Ar), 136.7 (Ar), 132.7 (Ar), 132.0 (2 × ArH), 131.1 (2 × ArH), 129.7 (2 × ArH), 128.9 (2 × ArH), 127.5 (2 × ArH), 127.1 (2 × ArH), 125.2 (2 × ArH), 121.7 (pyrrole), 121.6 (pyrrole), 120.2 (pyrrole CH), 119.4 (pyrrole), 115.1 (C≡N), 113.7 (2 × ArH), 109.0 (Ar), 55.1 (OCH_3), 21.4 (CH_3) and 21.0 (CH_3); HRMS (ESI-TOF) *m*/*z* $[M + H]^+$ calcd for $C_{32}H_{28}N_3O_3S^+$ 534.1846; found 534.1851.

*1,4-Di(4-tolyl)-2-(4-methoxyphenyl)-5-methyl-3-tosylaminopyrrole (**18t**).* 1-Ethynyl-4-methoxybenzene (43 μL, 0.32 mmol, 1.1 equiv) and 4-toluenesulfonyl azide (66 mg, 0.33 mmol, 1.1 equiv) were treated with CuTC (3 mg, 16 μmol, 5 mol %) in CH_2Cl_2 (10 mL), followed by α-aminoketone **16g** (76 mg, 0.30 mmol, 1.0 equiv) and $Rh_2(OAc)_4$ (1 mg, 2.3 μmol, 1 mol %), and finally $BF_3{\cdot}OEt_2$ (111 μL, 0.90 mmol, 3.0 equiv) according to General Procedure 5 to give the title compound **18t** (118 mg, 73%) as an orange solid: mp 70 °C dec; ν_{max} (film) 3275, 2920, 2851, 1512, 1462, 1381, 1323, 1246, 1157, 1092, and 1030 cm^{-1}; ^1H NMR (400 MHz, 25.0 °C, $CDCl_3$) δ 7.20 (2 H, d, *J* = 7.4 Hz, Ar), 7.13−7.05 (6 H, m, Ar), 6.96 (2 H, d, *J* = 8.1 Hz, Ar), 6.88 (2 H, d, *J* = 8.6 Hz, Ar), 6.82 (2 H, d, *J* = 8.1 Hz, Ar), 6.59 (2 H, d, *J* = 8.6 Hz, Ar), 6.03 (1 H, s, NH), 3.74 (3 H, s, OCH_3), 2.36 (3 H, s, CH_3), 2.32 (3 H, s, CH_3), 2.29 (3 H, s, CH_3) and 2.01 (3 H, s, CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, 25.0 °C, $CDCl_3$) δ 158.2 (Ar), 142.1 (Ar), 137.3 (Ar), 137.2 (Ar), 135.9 (Ar), 135.3 (Ar), 131.4 (Ar), 131.2 (2 × ArH), 130.8 (Ar), 129.5 (2 × ArH), 129.4 (2 × ArH), 128.8 (2 × ArH), 128.6 (2 × ArH), 128.3 (2 × ArH), 127.0 (2 × ArH), 125.7 (pyrrole), 123.4 (pyrrole), 120.4 (pyrrole), 114.5 (pyrrole), 113.2 (2 × ArH), 55.0 (CH_3), 21.4 (CH_3), 21.2 (CH_3), 21.1 (CH_3) and 11.9 (CH_3); HRMS (ESI-TOF) *m*/*z* $[M + H]^+$ calcd for $C_{33}H_{33}N_2O_3S^+$ 537.2206; found 537.2207.

*4-Cyclopropyl-1,2-di(4-tolyl)-3-tosylaminopyrrole (**18u**).* 4-Ethynyltoluene (43 μL, 0.37 mmol, 1.2 equiv) and 4-toluenesulfonyl azide (66 mg, 0.33 mmol, 1.1 equiv) were treated with CuTC (3 mg, 16 μmol, 5 mol %) in CH_2Cl_2 (10 mL), followed by α-aminoketone **16u** (57 mg, 0.30 mmol, 1.0 equiv) and $Rh_2(OAc)_4$ (1 mg, 2.3 μmol, 1 mol %), and finally $BF_3{\cdot}OEt_2$ (111 μL, 0.90 mmol, 3.0 equiv) according to General Procedure 5 to give the title compound **18u** (70 mg, 51%) as a yellow solid: mp 66 °C dec; ν_{max} (film) 3271, 3005, 2924, 2862, 1516, 1323, and 1161 cm^{-1}; ^1H NMR (400 MHz, 25.0 °C, $CDCl_3$) δ 7.37 (2 H, d, *J* = 8.3 Hz, Ar), 6.98 (2 H, d, *J* = 7.8 Hz, Ar), 6.91 (2 H, d, *J* = 8.3 Hz, Ar), 6.82 (2 H, d, *J* = 8.1 Hz, Ar), 6.81 (2 H, d, *J* = 7.8 Hz, Ar), 6.59 (2 H, d, *J* = 8.1 Hz, Ar), 6.39 (1 H, d, *J* = 0.8 Hz, pyrrole CH), 6.14 (1 H, s, NH), 2.30 (3 H, s, CH_3), 2.27 (3 H, s, CH_3), 2.26 (3 H, s, CH_3), 1.85 (1 H, ttd, *J* = 8.3, 5.2, 0.8 Hz, cyclopropane CH), 0.82 (2 H, ddd, *J* = 8.3, 6.1, 4.0 Hz, 2 × cyclopropane CH) and 0.51 (2 H, ddd, *J* = 6.1, 5.2, 4.0 Hz, 2 × cyclopropane CH); $^{13}C\{^1H\}$ NMR (101 MHz, 25.0 °C, $CDCl_3$) δ 142.5 (Ar), 137.6 (Ar), 136.8 (Ar), 136.4 (Ar), 136.0 (Ar), 130.2 (Ar), 129.5 (2 × ArH), 129.3 (2 × ArH), 128.8 (2 × ArH), 128.5 (2 × ArH), 127.3 (pyrrole), 127.2 (2 × ArH), 126.3 (pyrrole), 125.1 (2 × ArH), 117.6 (pyrrole), 116.9 (pyrrole CH), 21.5 (CH_3), 21.2 (CH_3), 20.9 (CH_3), 7.6 (2 × cyclopropane CH_2) and 5.7 (cyclopropane); HRMS (ESI-TOF) *m*/*z* $[M + H]^+$ calcd for $C_{28}H_{29}N_2O_2S^+$ 457.1944; found 457.1943.

*1,2-Di(4-tolyl)-4-(2-tolyl)-3-tosylaminopyrrole (**18v**).* 4-Ethynyltoluene (43 μL, 0.37 mmol, 1.2 equiv) and 4-toluenesulfonyl azide (66 mg, 0.33 mmol, 1.1 equiv) were treated with CuTC (3 mg, 16 μmol, 5 mol %) in CH_2Cl_2 (10 mL), followed by α-aminoketone **16v** (72 mg, 0.30 mmol, 1.0 equiv) and $Rh_2(OAc)_4$ (1 mg, 2.3 μmol, 1 mol %), and finally $BF_3{\cdot}OEt_2$ (111 μL, 0.90 mmol, 3.0 equiv) according to General Procedure 5 to give the title compound **18v** (82 mg, 54%) as a yellow solid: mp 80 °C dec; ν_{max} (film) 3271, 3063, 2924, 1516, 1389, 1327, and 1161 cm^{-1}; ^1H NMR (400 MHz, 25.0 °C, $CDCl_3$) δ 7.19 (2 H, d, *J* = 8.3 Hz, Ar), 7.15−7.04 (6 H, m, Ar), 7.01−6.98 (4 H, m, Ar), 6.97 (2 H, d, *J* = 8.3 Hz, Ar), 6.82 (2 H, d, *J* = 7.8 Hz, Ar), 6.69 (1 H, s, pyrrole CH), 6.08 (1 H, s, NH), 2.31 (6 H, s, 2 × CH_3), 2.29 (3 H, s, CH_3) and 2.23 (3 H, s, CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, 25.0 °C, $CDCl_3$) δ 142.2 (Ar), 137.5 (2 × Ar), 136.8 (Ar), 136.4 (Ar), 136.2 (Ar), 133.3 (Ar), 131.0 (pyrrole), 130.5 (ArH), 130.1 (2 × ArH), 129.9 (ArH), 129.5 (2 × ArH), 128.8 (2 × ArH), 128.8 (2 × ArH), 127.4 (Ar), 126.8 (2 × ArH), 126.5 (ArH), 125.4

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(ArH), 125.2 (2 × ArH), 122.6 (pyrrole), 120.3 (pyrrole CH), 116.3 (pyrrole), 21.4 (CH_3), 21.3 (CH_3), 20.9 (CH_3) and 20.7 (CH_3); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{32}H_{31}N_2O_2S^+$ 507.2101; found 507.2111.

*1,4-Di(4-tolyl)-2-(4-fluorophenyl)-3-tosylaminopyrrole (**18w**).* 1-Ethynyl-4-fluorobenzene (40 mg, 0.33 mmol, 1.1 equiv) and 4-toluenesulfonyl azide (66 mg, 0.33 mmol, 1.1 equiv) were treated with CuTC (3 mg, 16 μmol, 5 mol %) in CH_2Cl_2 (10 mL), followed by α-aminoketone **16a** (72 mg, 0.30 mmol, 1.0 equiv) and $Rh_2(OAc)_4$ (1 mg, 2.3 μmol, 1 mol %), and finally $BF_3{\cdot}OEt_2$ (111 μL, 0.90 mmol, 3.0 equiv) according to General Procedure 5 to give the title compound **18w** (134 mg, 87%) as a yellow solid: mp 90 °C dec; ν_{max} (film) 3275, 3024, 2920, 2866, 1510, 1505, 1412, 1389, 1323, 1223, 1157, and 1092 cm^{-1}; ^1H NMR (400 MHz, 25.0 °C, $CDCl_3$) δ 7.29−7.23 (4 H, m, ArH), 7.08−7.04 (2 H, m, ArH), 7.06 (2 H, d, J = 7.9 Hz, ArH), 6.99 (2 H, dd, J = 8.8, 5.4 Hz, C_6H_4F), 6.93 (2 H, d, J = 8.3 Hz, Ar), 6.86 (1 H, s, pyrrole CH), 6.83 (2 H, d, J = 7.9 Hz, ArH), 6.81 (2 H, dd, J = 8.8, 8.8 Hz, C_6H_4F), 6.21 (1 H, app d, J = 8.5 Hz, NH), 2.35 (3 H, s, CH_3), 2.32 (3 H, s, CH_3) and 2.28 (3 H, s, CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, 25.0 °C, $CDCl_3$) δ 161.9 (d, J = 247.2 Hz, C_6H_4F), 142.6 (Ar), 137.1 (Ar), 137.1 (Ar), 136.8 (Ar), 135.7 (Ar), 131.9 (d, J = 8.2 Hz, 2 × C_6H_4F), 131.0 (pyrrole), 130.8 (Ar), 129.6 (2 × ArH), 129.0 (2 × ArH), 128.8 (2 × ArH), 127.4 (2 × ArH), 127.0 (2 × ArH), 126.4 (d, J = 3.4 Hz, C_6H_4F), 125.3 (2 × ArH), 123.7 (pyrrole), 119.6 (pyrrole CH), 115.6 (pyrrole), 115.0 (d, J = 21.6 Hz, 2 × C_6H_4F), 21.4 (CH_3), 21.2 (CH_3) and 20.9 (CH_3); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{31}H_{28}FN_2O_2S^+$ 511.1850; found 511.1856.

*3-Amino-1,2,4-tri(4-tolyl)pyrrole (**23a**).* Triflic acid (16 μL, 0.18 mmol, 3.0 equiv) was added to a solution of pyrrole **18a** (30 mg, 0.059 mmol, 1.0 equiv) in 1,2-dichloroethane (2.0 mL) at 0 °C (ice bath). The mixture was heated at 90 °C (heating block) in a sealed vial for 2.5 h. The reaction mixture was cooled to ambient temperature, and the reaction was quenched by the addition of ethylenediamine (2 drops) followed by 1 M aqueous NaOH (2.0 mL). The aqueous phase was extracted with dichloromethane (3 × 2.0 mL), and the combined organic layers were washed with brine, dried ($MgSO_4$), and concentrated in vacuo. Purification by flash column chromatography (SiO_2, 5% hexane in ethyl acetate) gave the title compound **23a** (16 mg, 77%) as a yellow oil: ν_{max} (film) 3402, 3322, 3028, 2920, 2859, 1516, and 1389 cm^{-1}; ^1H NMR (400 MHz, 25.0 °C, $CDCl_3$) δ 7.52 (2 H, d, J = 8.1 Hz, Ar), 7.23 (2 H, d, J = 7.7 Hz, Ar), 7.12−7.00 (8 H, m, Ar), 6.85 (1 H, s, pyrrole CH), 3.35 (2 H, br s, NH), 2.38 (3 H, s, 2 × CH_3) and 2.32 (6 H, s, CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, 25.0 °C, $CDCl_3$) δ 138.1 (Ar), 135.4 (Ar), 135.4 (Ar), 135.3 (Ar), 131.9 (pyrrole), 129.5 (2 × ArH), 129.5 (2 × ArH), 129.2 (3 × ArH and Ar), 128.9 (2 × ArH), 128.6 (pyrrole), 127.1 (2 × ArH), 124.5 (2 × ArH), 119.2 (pyrrole CH), 117.9 (Ar), 116.9 (pyrrole), 21.2 (CH_3), 21.1 (CH_3) and 20.9 (CH_3); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{25}H_{25}N_2^+$ 353.2012; found 353.2014.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.2c00434.

High-resolution ^1H and ^{13}C NMR spectra of all products and selected NOESY spectra (PDF)

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The manuscript was written through contributions of all authors.

Notes

The authors declare no competing financial interest.

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